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Final Report

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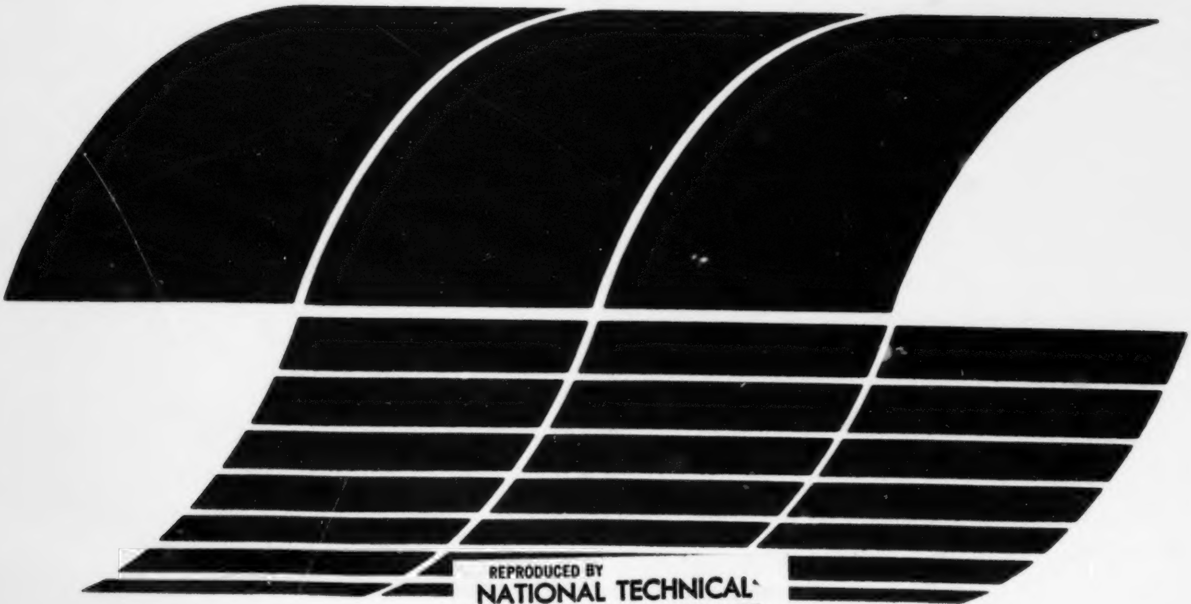

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Flue Gases	Ponds	Stationary Sources	21B	08H
Desulfurization	Earth Fills	Nonregenerable Systems	07A, 07D	13C
Waste Disposal	Gypsum	Double Alkali Process		
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Disposal of By-products from Nonregenerable Flue Gas Desulfurization Systems:
Final Report

by

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Washington, DC 20460

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ABSTRACT

This report provides results of a four-year study by The Aerospace Corporation to determine environmentally sound methods for the disposal of wastes from nonregenerable flue gas desulfurization systems. The data presented incorporate the results obtained during the fourth year of the study and the material presented in the second progress report, EPA-600/7-77-052, May 1977, which covered the first three years of the study. Untreated and treated wastes from ten different scrubbers at Eastern and Western plants using lime, limestone, and double alkali processes are characterized. The report relates concentrations of salts and trace elements in the wastes to the potential for water pollution. Physical properties, e.g., bulk density, load-bearing strength, permeability, and viscosity are given. Disposal by means of ponding, landfilling of chemically fixed wastes, ponding with underdrainage, and conversion to gypsum are assessed. Disposal cost estimates for a 1000-MW Eastern plant are 0.55, 0.90, and 1.20 mills/kWh for ponding on indigenous clay, ponding with liner added, and chemical treatment/landfill, respectively.

Companion studies within this contract pertaining to field disposal evaluations and a summary of all U.S. Environmental Protection Agency projects related to flue gas desulfurization waste and water studies, have been reported in separate documents.

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CONVERSION TABLE

British	Metric
1 inch	2.54 centimeters
1 foot	0.3048 meter
1 mile	1.609 kilometers
1 square foot	9,290 square centimeters
1 acre	4,047 square meters
1 cubic foot	28,316 cubic centimeters
1 gallon	3.785 liters
1 cubic yard	0.7646 cubic meter
1 pound	0.454 kilogram
1 ton (short)	0.9072 metric ton
1 pound per square inch	0.0703 kilogram per square centimeter
1 pound per cubic foot	0.01602 gram per cubic centimeter
1 ton per square foot	9,765 kilograms per square meter
1 part per million	1 milligram per liter (equivalent)
1 British thermal unit (Btu)	252 calories
1 pound per million Btu	0.43 grams per million joules; 1.80 grams per million calories
1 Btu per pound	2.324 joules per gram; 0.555 calorie per gram

SECTION I

INTRODUCTION

1.1 REPORT COVERAGE

This is the third and final report on a study of the disposal of the by-products from nonregenerable flue gas desulfurization (FGD) systems. The total study spans the period of 1973 through mid-1977. This document contains a summary of the results of the total effort, which consisted of engineering studies, laboratory experimentation, and data assessments. This document also includes detailed technical discussions of work performed from January 1976 through March 1977 (with some updating made during the report writing effort). The most recent efforts consisted of studies of the physical and chemical characteristics of sludge samples from three different scrubber facilities: (1) the Tennessee Valley Authority's (TVA) Shawnee Steam Plant, (2) Louisville Gas and Electric Company's Paddy's Run Station, and (3) Gulf Power Company's Plant Scholz. Studies were made, also, of gypsum produced by forced oxidation at the U.S. Environmental Protection Agency's (EPA) Research Triangle Park pilot plant, and cost estimates for a commercial-scale forced oxidation system similar to EPA's were made. The environmental acceptability of FGD sludge was reviewed, and studies were expanded to include ponding of untreated sludges in basins with underdrainage systems which return all seepage to the scrubber. Previous cost estimates were updated to reflect a 1977 dollar cost basis.

Prior reports on this study (Refs. 1 and 2) have included results of analyses which were conducted on samples obtained from seven different scrubber systems. This report serves to expand the data base reported on previously by examining the properties of (1) lime scrubbing sludge without fly ash, (2) carbide lime waste as an absorbent scrubbing sludge, and (3) double alkali sludge with and without fly ash.

Other phases of this program, i.e., the EPA/TVA Shawnee field disposal evaluation project and a review of all Research and Development (R and D) activities concerning the disposal of flue gas cleaning waste materials were reported on separately (Refs. 3 through 6). A third annual report on the field evaluation project is in work.

1.2 OBJECTIVES AND STUDY APPROACH

The specific objectives of this study are as follows:

a. To identify environmental problems associated with FGD waste disposal by determining FGD waste chemical and physical characteristics.

b. To assess current FGD waste disposal methods, including feasibility, performance, and costs, by conducting laboratory studies of wastes under conditions associated with waste disposal, by providing engineering support and conducting chemical and physical analyses for the Shawnee field disposal evaluation, by evaluating other available data, and by conducting engineering cost studies of disposal methods.

c. To identify alternative disposal methods that provide an acceptable means of FGD waste disposal by cost-effective methods.

d. To make recommendations regarding alternative disposal approaches.

The objectives of this study were met by (1) reviewing water quality standards and waste management regulations and correlating this study's technical evaluations with potential limitations imposed by these regulations, as appropriate; (2) performing analyses to determine chemical and physical characteristics, as appropriate, of FGD wastes, coals, makeup water, fly ash, and chemically treated wastes from EPA-specified sources; (3) surveying and analyzing technical and economic data pertaining to FGD waste disposal; (4) planning, coordinating, evaluating, and reporting the EPA field disposal evaluation at TVA Shawnee (Ref. 4); and (5) making recommendations for environmentally sound FGD waste disposal techniques.

1.3 ORGANIZATION OF REPORT

Sections II and III provide conclusions and recommendations, respectively. Section IV summarizes the total study findings and provides discussions and appropriate tables and figures to support the findings. Sections V through X comprise the total technical discussion of the work performed during this reporting period.

Appendix A provides a description of crystal morphology pertaining to the sludge samples analyzed during this reporting period.

SECTION II

CONCLUSIONS AND FINDINGS

2.1 CONCLUSIONS

These conclusions are based on results of the total study discussed herein and include, as appropriate, inputs from two tasks that are reported on separately, i.e., the EPA/Aerospace/TVA Shawnee field disposal evaluation project and an Aerospace summary of EPA's research and development programs for the control of waste and water pollution from power plant flue gas cleaning (FGC) systems. It should be noted that these conclusions are made in the absence of federal criteria pertaining to scrubber sludge disposal.

2.1.1 Characterization

Sludges have been characterized physically and chemically. These analyses have shown the need to avoid potential water pollution and land degradation problems.

2.1.2 Disposal Methods

2.1.2.1 Chemical Treatment

It has been shown that sludges which have been chemically treated by commercially available processes can be disposed of in an environmentally sound manner and that the disposal site can be reclaimed as a structural landfill. Chemically treated sludge disposal sites which are basically "dry disposal" operations must be managed to control runoff throughout the disposal operation, after which they must be covered with earth and vegetation. Such site management is necessary to prevent the discharge of eroded material or dissolved solids into adjacent waterways or contiguous land surfaces. Chemically treated sites which are classified as "underwater" disposal must be located in an impoundment area for which the local hydrological and geological characteristics and history are well known so that any seepage, overflow, or discharge can be accommodated by the soil and/or adjacent streams and so that any buildup of sludge constituents, under worst case conditions, is not appreciable when judged by local regulations. During the period of preparation of this report, several full-scale chemically treated sludge disposal sites, both dry and underwater, have become operational. These are being monitored for environmental control, and to date no deficiencies have been reported.

2.1.2.2 Ponding

Ponding of untreated sludge on a site containing indigenous or transported soil considered effective as an impervious base having a coefficient of permeability of approximately 10^{-7} or better has been demonstrated (both in test sites and operationally) to be effective for the control of seepage and overflow during the period of operation; however, sites such as these are not considered amenable to land reclamation. Furthermore, serious doubt exists as to the acceptability of ponding particularly because of the nonstructural nature of the pond. In this regard, it should be noted that the EPA has taken one position with respect to sludge disposal in its draft response to a remand issued on September 10, 1973 by the U. S. Court of Appeals for the District of Columbia:

> EPA considers permanent land disposal of raw (unfixated) sludge to be environmentally unsound, because it indefinitely degrades large quantities of land. Although EPA has no regulatory authority to prevent raw sludge disposal, EPA anticipates States and local jurisdictions to require treatment of sludge . . .

Preventing the degradation of large quantities of land appears to be the intent.

2.1.2.3 Conversion to Gypsum

The process of forced oxidation of sulfite sludges within the scrubber loop produces a gypsum by-product which can be filtered to a high solids content material that is easily handled. Because most of the water is removed in the dewatering process, a smaller mass of material is produced for disposal. Advantages exist also within the scrubber loop in that the size of settling tanks is reduced because of the fast settling property of gypsum, and the process tends to afford total utilization of the limestone. As of this writing, sludge is converted to gypsum and disposed of, at one operational site, in an enclosed basin lined with clay which has been transported to the disposal site. Further tests are being conducted at the Shawnee field disposal site to evaluate environmental effects, site maintenance requirements, and amenability of the material for landfill utilization.

2.1.2.4 Ponding with Underdrainage

A method by which untreated sludge is disposed of in an enclosed basin that is equipped with an underdrainage system is being evaluated at the EPA/TVA Shawnee field disposal site. This method facilitates quick settling and densification of the sludge and returns all underdrainage to the scrubber. No operational site is using this approach; however it shows promise for producing a structurally sound ponding material which would be amenable to land reclamation and which may not require a very low permeability base material. Evaluations are continuing on this method of disposal.

2.1.2.5 Mine Disposal

Disposal of sludges in mines, particularly coal mines, appears attractive and is being evaluated separately under EPA sponsorship. Currently, one disposal site is operational in an active surface mine area (Milton R. Young Power Station Center, North Dakota, a mine mouth station), and another site is operational in a manner similar to that appropriate for mine disposal (Martin Lake, Tatum, Texas). Both of these sites are in lignite coal areas, and the sludge is dewatered prior to disposal but not chemically treated.

At the Milton R. Young Station, the fly ash, which is a highly alkaline material, is collected, slurried, and used as a scrubbing reagent with lime supplement. All hauling of coal and sludge is by truck. The sludge is filtered and disposed of both in the pit area and between spoil banks (V-notch). The EPA is supporting a detailed monitoring effort conducted by the University of North Dakota and the North Dakota State Geological Survey. This includes groundwater monitoring, characterization of the waste material, core sampling, and soil sampling.

At the Martin Lake Station, limestone is used as the absorbent in the scrubber, and the sludge is blended with fly ash for dewatering. This sludge is transported by train to a landfill which is not an active mine area, but may be in the future. If so, the sludge may be mixed with overburden.

2.1.2.6 Ocean Disposal

Ocean disposal is being studied under separate EPA sponsorship to better understand the potential effects of the chemical and physical characteristics of chemically treated and untreated sludges on the ocean environment. At Stonybrook, Long Island, New York, the New York State Energy Research and Development Authority and New York State University are building small artificial reefs of chemically treated sludge blocks to perform biological tests and to determine the structural integrity of the treated materials. No detrimental effects have been determined, and monitoring is continuing. Additionally, the New England Aquarium is conducting biological tests and chemical analyses of chemically treated sludges immersed in an aquarium.

2.1.3 Sludge Utilization

2.1.3.1 Alumina Extraction

A separate economic study, under EPA sponsorship, of an alumina extraction process utilizing FGC waste as a source of calcium has been completed, and the limitations under which this method of utilization may be competitive with bauxite have been defined. Several key processing steps have also been identified that require experimental verification. In general, this process doesn't appear to be economically practical without an adjoining cement plant which could utilize one of the by-products of the process.

2.1.3.2 Gypsum

Chemical and physical characteristics of pilot-plant-produced gypsum by forced oxidation have been determined. Engineering estimates have indicated that the cost of saleable gypsum produced by this process can be competitive with domestically mined crude gypsum if appropriate cost avoidance credits are taken for chemical treatment and disposal. The marketability of this material requires further study, which is being conducted by TVA under EPA sponsorship.

2.1.4 Economics of Disposal (Sludge Including Fly Ash)

The mid-1977 cost of disposal in the following conditions, ponding on indigenous clay, ponding with liner added, and chemical treatment/landfill, were estimated to be 0.55, 0.8, and 1.05 mills/kWh, respectively. This equates to \$4.90, \$7.25, and \$9.70 per ton of sludge on a dry basis, and \$1.50, \$2.20, and \$2.95 per ton of coal burned.

The cost of gypsum disposal including the forced oxidation of the sulfite sludge, filtration, and disposal of the gypsum including ash, in an indigenous clay basin, was estimated to be 1.05 mills/kWh. On the basis of an equivalent quantity of nonoxidized sludge, this value is 1.10 mills/kWh.

2.2 FINDINGS

A brief discussion of findings regarding the chemical and physical characteristics of sludges is as follows.

2.2.1 Leachate Chemistry

In the absence of federal disposal criteria (which are now being developed under provisions of the Resource Conservation and Recovery Act of 1976), drinking water criteria specified under the National Interim Primary Drinking Water Regulations were used as a basis for determining the necessity for protecting water supplies from intrusion by seepage or leachate from disposal sites. The trace element and major anion content (arsenic, cadmium, chromium, lead, mercury, selenium, fluoride, chloride, and sulfate) of most samples analyzed exceeded the criteria at least for some of these constituents, as did pH and chemical oxygen demand (COD).

2.2.2 Physical Properties

2.2.2.1 Bearing Strength

Although no criteria are specified for the strength required for sludges in a disposal site, tests were made at the field evaluation disposal site to determine the load-bearing capability of various sludges in differing disposal modes and to verify the capability of these materials to support construction equipment.

In-situ penetrometer tests at the Shawnee disposal test sites showed bearing strengths in the range of 100 to 300 psi for the chemically treated sludges, and the following values for untreated-underdrained sludge slurries: limestone, 60 to 75 psi; lime, 100 to 240 psi; and gypsum, 300 psi. All of these sites, except the untreated-underdrained limestone sludge site, supported moving rubber-tired construction vehicles having tire pressures of 95 psi. The underdrained limestone site supported a moving vehicle carrying tire pressures of 22 psi. These are not necessarily the maximum tire pressure capabilities of these materials, but are further indications of the variations in strength.

The ability to compact gypsum filter cake and its subsequent load bearing strength are to be determined at the field site.

2.2.2.2 Wet Bulk Density

Wet bulk densities increase in the following order according to the dewatering method used: (1) settled, (2) drained, and (3) filtered/centrifuged. Densities also increase with the type of absorbent used, in the following order: (1) lime or double alkali and (2) limestone. The presence of fly ash in lime and limestone sludges causes a minor increase in density over that of sludges without fly ash. For double alkali systems, the differences in wet bulk density for sludges with and without ash are smaller and varied enough that no definite trend was established. In general, wet bulk density in the settled condition ranged between approximately 1.3 and 1.45 g/cc except for gypsum, which was 1.65; for the drained case, the variation was between 1.3 and 1.53 except for gypsum, which was 1.67; and for the filtered or centrifuged cases the variation was between approximately 1.45 and 1.65 except for gypsum, which reached values as high as 1.86.

2.2.2.3 Coefficient of Permeability

The permeability coefficient of untreated sludges is typically 10^{-4} cm/sec although some untreated samples were found to have coefficients as low as 2×10^{-5} and as high as 9×10^{-4}. When placed in a disposal basin which is provided with underdrainage, a 40-ft impoundment consolidates such that a permeability coefficient at the lower level decreases to approximately 10^{-5} cm/sec. It was found that compaction of untreated dewatered sludges decreases the permeability coefficient by approximately one order of magnitude under a pressure of 30 psi.

Chemically treated sludges typically have a permeability coefficient of 10^{-5} or less. During the course of this study, pulverized or fractured samples were also tested and shown to have coefficients of as high as 10^{-4} cm/sec. However, stabilized samples extracted from the Shawnee disposal site verify the typical value of 10^{-5}, with some samples having coefficients as low as 10^{-7}.

2.2.2.4 Viscosity

Pumpability (<20 poise), determined by laboratory viscosity tests, was found for various untreated sludges which had maximum solids content that ranged between 32 and 70 percent. For all samples analyzed, each had a critical value of solids content at which the viscosity increased steeply. However, in general at any given solids content, the double alkali and carbide lime sludges were the most viscous; lime sludges were somewhat less; and the limestone sludges were the least. Double alkali ash-free sludges were considered pumpable at a solids content of less than about 30 wt %; lime and limestone ash-free, at solids content of less than about 40 wt %; and all sludges with ash, at a maximum solids content in the range of 40 to 50 wt %.

2.2.3 Chemical Properties

The typical level of total dissolved solids (TDS) in FGD sludge liquors analyzed in this work was approximately 10,000 mg/ℓ (steady state) except for double alkali scrubbers, whose liquors have a much higher TDS. The distribution of trace metals in systems liquors tends to lie between 0.01 and 1 mg/ℓ or ppm for all elements except mercury, which has a concentration distribution about 1/10 that of other trace elements. In most sludge liquors, pH ranges between 6.5 and 9; however, in some samples, pH in the 10 to 12 range were detected. COD ranged between 40 and 140 mg/ℓ.

The concentration of major chemical species increases with time from startup until a steady-state condition is reached for all species. Trace element concentrations reach steady state rapidly and are not affected by the steady-state conditions of the major species.

The scrubber pH seems to be responsible for trace metals leaching from fly ash. The pH of the system downstream of the scrubber does not significantly affect the concentration of trace elements in the scrubber liquor.

A direct correlation exists between the trace element and chlorine content of coal and the trace element and chloride content in FGD sludges.

Fly ash represents the major source of trace elements in all but the most volatile species (e.g., mercury and selenium) that are scrubbed from the flue gases.

Western coal, having typically lower concentrations of arsenic, cadmium, mercury, and zinc than Eastern coal, generally produces sludge having lower concentrations of these elements than does Eastern coal.

2.2.4 Chemical Solubility

For the nine trace elements measured extensively in this study (arsenic, cadmium, chromium, lead, mercury, selenium, zinc, beryllium, and copper), there was no evidence that trace element saturation was the controlling parameter for the trace material concentration in the liquor.

2.2.5 Pilot Plant Forced Oxidation of Sulfite Sludges

Analyses were made of gypsum produced by forced oxidation of sulfite sludge in an EPA pilot plant to augment limestone and gypsum settling rate tests being performed by EPA. Results were as follows:

a. Permeability coefficient was approximately 1×10^{-4} cm/sec.

b. Pore volume fraction was 0.55 and 0.5 for gypsum without and with fly ash, respectively. Wet bulk densities were 1.3 and 1.4 g/cm^3, respectively, when settled and drained, and without compaction.

c. Unconfined compressive strength was approximately 60 psi. The presence of as little as 5 percent sulfite reduced this value to 15 psi.

d. Gypsum filtered to approximately 85 percent solids.

e. Leachate after 2 to 3 pore volume displacements of water was saturated with calcium and sulfate ions.

SECTION III

RECOMMENDATIONS

Because of the wide variations in the chemical and physical characteristics of flue gas desulfurization (FGD) sludges as produced and in their application to various disposal or utilization techniques, certain parameters, such as scrubber operating conditions as they affect crystal size, shape, and distribution; freeze-thaw and wet-dry effects; runoff conditions as they affect chemically treated sludges; and alternative disposal methods, need a broader data base than now available. A broader data base would enhance the ability to control the characteristics of sludge as well as predict and control the response of the sludge to environmental, land reclamation, or utilization applications. The net effect would be a technological base which would broaden the applications range of these materials and in many cases simplify operational procedures which would both improve reliability and reduce costs. The following recommendations are made in that regard.

3.1 FIELD DISPOSAL EVALUATION PROGRAMS

Current programs should be continued, particularly those that broaden the data base with extended time data incorporating the combined effects of time, temperature, moisture, and freeze-thaw/wet-dry cycling on chemically treated and untreated sludges. Evaluations to determine simple, low-cost methods of gypsum disposal should be continued, as well as low-cost underdrainage systems for ponds to contain untreated sludges.

3.2 CHEMICALLY TREATED SLUDGES

Further testing should be conducted on chemically treated sludges for conditions simulating rainfall runoff from landfills on which uncured treated sludge is continually added. Further testing of slope strength of chemically treated sludges should also be conducted.

3.3 CONTROL OF SLUDGE CRYSTALLINE STRUCTURE

Scrubber sludges having a high sulfite to sulfate ratio exhibit undesirable characteristics regarding disposal because, in general, they are

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highly water-retentive and have low settling rates and settled strength when compared to these characteristics of sludges having high sulfate to sulfite ratios. These characteristics of the high sulfite sludges are a result of the thin platelet structural geometry of the crystals; additionally, their characteristics are difficult to predict because of the wide variations in crystalline size and shapes that result from the use of different coals, absorbents, scrubber systems, and scrubber operating parameters. It is recommended that an experimental program be conducted to identify scrubber operating procedures which would produce crystalline structure that would enhance disposal characteristics, with special attention being given to thickening the platelet structure of high sulfite sludges.

SECTION IV

SUMMARY

4.1 GENERAL

A summary highlighting results of the total effort of this program to date is presented in this section. Brief discussions of each area of investigation are given, and selected figures and tables are included to either simplify the summary or to provide the data necessary to complete the discussions. Some of these figures and tables are repeated in the appropriate sections of the body of the report when necessary to complete the detailed technical description therein.

These summary results consist of an integration of data obtained during the current reporting period with all data derived previously and reported in References 1 and 2. Sources of materials analyzed are identified in Table 1; those analyzed during the current reporting period were obtained from Plants 8 through 11. It should be noted that the flue gas desulfurization (FGD) waste disposal studies that were initiated in this program are now concentrated in an ongoing field disposal evaluation project at the U. S. Environmental Protection Agency/Tennessee Valley Authority (EPA/TVA) Shawnee test site in Paducah, Kentucky. Annual reports on that project will be published in addition to References 3 and 4.

4.2 DISPOSAL CRITERIA

Throughout the study, in the absence of federal or other criteria relating directly to the disposal of FGD sludges, drinking water criteria have been used as a basis for establishing requirements for disposal. Because the trace element and salt content of most samples analyzed exceeded the drinking water criteria, at least for some of the constituents, the approach taken in this study has been to consider disposal of the FGD sludges such that no direct discharge to any water supply would be allowed and that any seepage or runoff would be minimized or perhaps totally eliminated. Various methods of disposal have been studied and evaluated in the field (Refs. 3 and 4) and are discussed in Section IX.

TABLE 1. FGD SYSTEMS SAMPLED AS DATA BASE

	Power Plant	Scrubber System	Scrubbing Capacity, MW Equivalent	Coal Source	Absorbent
1.	Tennessee Valley Authority (TVA) Shawnee Steam Plant	Venturi and spray tower, prototype	10	Eastern	Lime
2.	TVA Shawnee Steam Plant	Turbulent contact absorber, prototype	10	Eastern	Limestone
3.	Arizona Public Service (APS) Company, Cholla Power Plant	Flooded-disk scrubber, wetted film absorber	120	Western	Limestone, fly ash
4.	Duquesne Light Company (DLC), Phillips Power Station	Single- and dual-stage venturi	410	Eastern	Lime
5.	General Motors (GM) Corporation, Chevrolet-Parma Power Plant	Bubble-cap tower	32	Eastern	Soda ash, lime regenerant (double alkali)
6.	Southern California Edison (SCE) Mohave Generating Station	Turbulent contact absorber, pilot plant	< 1	Western	Limestone
7.	Utah Power and Light (UPL) Company, Gadsby Station	Venturi and mobile bed, pilot plant	< 1	Western	Soda ash, lime regenerant
8.	Gulf Power Company (GPC), Plant Scholz	Venturi and spray tower	20	Eastern	Soda ash, lime regenerant
9.	Louisville Gas and Electric (LG&E), Paddy's Run Station	Marble bed absorber	70	Eastern	Carbide, lime (slaked lime waste)
10.	EPA Pilot Plant, Research Triangle Park (RTP), NC	Two-stage scrubber	0.1	Simulated Eastern	Limestone
11.	TVA Shawnee Steam Plant Plant (same as item No. 1, but downstream of ash collectors)	Venturi and spray tower, prototype	10	Eastern	Lime

During the period of performance of the final phase of this study, the Resource Conservation and Recovery Act (RCRA), Public Law 94-580, was enacted (October 1976). Under the provisions of this act, the EPA has been directed to provide regulations and guidance to control the disposal of hazardous and nonhazardous wastes including solid waste, which includes FGD sludges (air pollution control sludges). Under the provisions of the RCRA, the EPA is to develop a definition of hazardous wastes. Under various criteria, "toxicity" will undoubtedly be included and could pertain to FGD sludges. If these sludges are defined to be hazardous, the generation, transportation, and disposal would be controlled by EPA regulations as a minimum. If the sludges are determined to be nonhazardous, disposal would be controlled under the provisions of the RCRA land disposal program. EPA would produce disposal guidelines but the responsibility for disposal would be that of the states.

At this time, the hazardous and nonhazardous definitions are still being formulated, and formal nonhazardous disposal guidelines have not been promulgated. Therefore, the environmental acceptability of FGD sludge disposal has been studied in terms of preventing or minimizing the pollution of groundwaters or surface streams, using the best practical technology available today, with consideration given to near-term disposal method improvements.

A comparison of the chemical constituents of sludge liquors in a discharge stream with the National Interim Primary Drinking Water Regulation (NIPDWR) is given in Table 2 as a ratio of constituent concentration to water criteria. These ratios are given for the ranges of constituents from all samples analyzed (Table 3), for six independent samples analyzed in the final phase of this study (Section VII), and for samples previously analyzed (Ref. 1). The values used in this comparative analysis represent the initial release of these constituents from the base of an untreated disposal site; continued leaching of a given sample would result in a reduction of concentrations.

In Table 2, the ratios for concentrations in the "Range of All Samples" column show that all elements analyzed plus the total dissolved solids (TDS) and pH exceed drinking water criteria. However, in observing ratios for the 10 independent samples shown in the table it can be seen that, except for selenium in two samples and cadmium in one, no trace element exceeds the criteria by a factor greater than 10. The TDS are excessive for most of the samples, and the pH is excessive for two. Although trace elements are not eliminated as a matter of concern by these data, there are indications that in many cases the concentrations are quite low and that the item for concern may generally be the concentration of dissolved solids and, in some cases, pH. It is difficult at this point, in consideration of potential experimental data variations, the depletion of the material with leaching time, cation exchange and adsorption in the soil, the dilution between the disposal site and the consumer tap, to specifically quantify the degree of pollution potential from the disposal of these sludges. Because of the comparatively large concentration of dissolved solids and the identification of random values of high concentrations of trace elements, methods to

TABLE 2. COMPARISON OF SLUDGE LIQUOR WITH DRINKING WATER CRITERIA

NIPDWR Drinking Water Criteria, mg/ℓ	Concentration ÷ Criteria (Nondimensional)										
	Range of All Samples	Sample[a]									
		A	B	C	D	E	F	G	H	I	J
As 0.05	< 0.8 - 2.8	0.6	0.4	2.0	0.04	0.4	1.2	2.8	0.1	0.8	0.2
Cd 0.01	0.4 - 11	5.0	1.2	0.4	--	11	1.3	--	--	5	2.5
Cr 0.05	0.22 - 5	5.0	0.8	1.8	--	0.6	0.2	--	--	--	1.1
Pb 0.05	0.2 - 6.6	0.8	3.0	4.6	<0.2	6.6	0.2	< 0.2	< 0.2	0.8	< 0.1
Hg 0.002	0.03 - 2.5	2.5	--	--	<0.1	< 0.5	< 0.001	< 0.1	< 0.1	0.1	0.03
Se 0.01	0.28 - 20	10.0	3.3	10.0	4.2	< 2	7.8	20	14	2.8	0.3
F ~2	< 0.5 - 5	--	0.5	3.3	--	1.7	1	--	--	5	< 0.5
TDS 500	6.6 - 48.5	36	6.6	30.0	13.4	18.8	20.5	28	18.4	8.4	48.5
pH (actual values)[b]	6.7 - 12.2	6.7	6.8	8.0	12.2	8.7	8.0	7.8	7.3	10.7	8.9

[a] Sample data are as follows:

Sample	Station	Absorbent	% Ash	Sampling Date
A	Mohave	Limestone	3	Mar 1973
B	Cholla	Limestone	59	Nov 1974
C	Shawnee	Limestone	40	Jun 1974
D	Shawnee	Limestone	6	Jan 1977
E	Shawnee	Lime	40	Jun 1974
F	Shawnee	Lime	6	Sep 1976
G	Shawnee	Lime	6	Oct 1976
H	Shawnee	Limestone[c]	6	Aug 1977
I	Duquesne Phillips	Lime	60	Jun 1974
J	LG&E Paddy's Run	Carbide lime	12	Jul 1976

[b] EPA-proposed secondary regulation is 6.5 to 8.5.

[c] Forced-oxidized to gypsum.

TABLE 3. RANGE OF CONCENTRATIONS OF CHEMICAL CONSTITUENTS IN FGD SLUDGE LIQUORS THROUGHOUT THE SCRUBBER LOOP – ALL SOURCES[a]

Scrubber Constituents	Sludge Liquors, mg/ℓ
Aluminum	0.03 to 2.0
Arsenic	0.004 to 0.14
Beryllium	0.001 to 0.18
Cadmium	0.004 to 0.11
Calcium	10 to 2600
Chromium	0.011 to 0.25
Copper	0.002 to 0.56
Lead	0.005 to 0.33
Magnesium	0.1 to 2750
Mercury	0.00005 to 0.005
Potassium	5.9 to 760
Selenium	0.0006 to 0.20
Sodium	10.0 to 55,000
Zinc	0.001 to 0.59
Chloride	420 to 33,000
Fluoride	0.6 to 10
Sulfate	600 to 84,000
Sulfite	0.9 to 3500
TDS	2800 to 162,700
pH	4.3 to 12.7
COD	40 to 140

[a] All test conditions not necessarily standard. See Table 2 for representative list.

dispose of these materials which will prevent their access to public water supply have been assessed. These include chemical treatment and landfilling, disposal in impermeable ponds, dry disposal of gypsum (produced by oxidation of calcium sulfite), and disposal in basins equipped with underdrainage. These methods are discussed in detail in Sections V and IX, which compare the degree of pollution control offered by each, and disposal costs.

4.3 PHYSICAL PROPERTIES

The physical properties measured in this study for the characterization of FGD sludges include wet bulk densities of the sludges as a function of dewatering processes, coefficient of permeability, viscosity as a function of water content, compactibility, bearing strength, and unconfined compressive strength as a function of moisture content. Further characterization included the identification of the crystalline phases in each sludge, the relative quantity of each phase, and the morphological description of each phase. In addition, sludge samples chemically treated by commercial processors were evaluated with respect to their coefficient of permeability and unconfined compressive strength. An interpretation of the resultant behavior of all experimental tests performed is made relative to the physical or chemical characteristics of each sludge, and an evaluation is made of these behavioral effects on the requirements for environmentally safe disposal.

4.3.1 Wet Bulk Density

The dewatering characteristics of FGD sludges are important to the various disposal techniques in that they affect the volume of the disposal basin, the methods of handling the sludges, and the condition of the sludges in their state of ultimate disposal. All of these variables affect the economics of disposal as well as the pollution potential of the resultant waste. The ability of a sludge to be dewatered is primarily a function of the size and distribution of particles and the morphology of the particles determined by the crystalline phase. In this study, four methods of dewatering were investigated in the laboratory: settling, settling with drainage, vacuum filtration, and centrifugation. These methods are those most often used or considered because of their relative cost effectiveness.

The results show that all dewatering behavior responds to a relationship that correlates the wet bulk density ρ_B of a material to the dry bulk density ρ_D, the weight fraction f_s, the true density ρ_s of the solid, and the density of water ρ_w by the equation:

$$\rho_B = \frac{\rho_s \rho_w}{\rho_w f_s + \rho_s (1 - f_s)}$$

This relationship corresponds to a condition in which the water content of the dewatered sludge exceeds the amount just necessary to fill the void spaces when the particles are closely packaged together. Each dewatering method and the characteristics of each sludge established a particle packing that can be determined by measuring the dry bulk density of the sludge when all water has been dried from the sample. If water is incrementally added to the dried sample, the wet bulk density increases relative to the dry bulk density ρ_D by the equation:

$$\rho_B = \frac{\rho_D}{f_s}$$

When sufficient water is added to just fill all void spaces between particles, the maximum density for the sludge ρ is reached and is defined as the coincidence of the two equations.

If the dewatering efficiency of each method is defined as the percent of the measured wet bulk density relative to the maximum density attainable, a means of comparing the efficiency of each method is available. In all cases, the highest dewatering efficiency was obtained by vacuum filtration (av 93.6 percent); and the lowest efficiency was by centrifugation (av 81.9 percent); settling (av 86.2 percent) and free drainage (av 87.2 percent) efficiencies lie in between. However, when actual wet bulk densities are compared, as in Table 4, little difference is seen between vacuum filtration and centrifugation, and in some cases centrifugation produces the most dense sludge among the four methods evaluated.

The discrepancy is explained by the difference in particle packing that results from each method. Centrifugation is a high force method that packs particles closely together, but when performed in a glass vial water is not efficiently removed from between the particles. Vacuum filtration is a method that uses considerably less force and may result in poor particle packing relative to the applied force. The vacuum-assist is most effective in removing the water from between the particles, and this is the primary source of the high dewatering efficiency. Settling with or without drainage is a low force method, and particle packing is generally poorest. The difference between these two methods is a consequence of the loss of some water by drainage.

When industrial filters and centrifuges are used rather than laboratory equipment, filtration is generally expected to be slightly less effective with a resultant decrease in dewatering efficiency. On the other hand, centrifugation is usually less effective in particle packing and more effective in removing water because of a difference in mechanism for separating water from solids. Thus, in field conditions, the efficiency of dewatering by these two methods is more nearly equivalent with a general tendency for centrifugation to provide more consistent results. Settling methods are always less effective than either filtration or centrifugation, but in many cases their use constitutes the most cost-effective dewatering method.

TABLE 4. SAMPLE SOURCES AND DENSITIES

Sample Source and Date	Fly Ash, wt %	Bulk Density, g/cc			
		Settled	Drained	Filtered	Centrifuged
TVA Shawnee Limestone, 2/1/73	20	1.45	1.51	1.65	1.56
TVA Shawnee Limestone, 6/15/74	40	1.46	1.53	1.64	1.60
TVA Shawnee Lime, 3/19/74	40	1.36	1.34	1.51	1.44
GM Parma Double Alkali, 7/18/74	7	1.31	1.35	1.52	1.43
UPL Gadsby Double Alkali, 8/9/74	9	1.33	1.30	1.50	1.62
DLC Phillips Lime, 6/17/74	60	1.40	1.48	1.52	1.52
APS Cholla Limestone, 9/1/74	59	1.39	1.44	1.48	1.58
SCE Mohave Limestone, 3/30/73	3	1.65	1.67	1.78	1.86
TVA Shawnee Lime, 9/8/76	6	1.37	1.42	1.49	1.39
TVA Shawnee Lime, 9/8/76	40	1.35	1.50	1.54	1.44
GPC Scholz Double Alkali, 6/20/76	0	1.35	1.44	1.61	1.38
GPC Scholz Double Alkali, 6/27/76	30	1.36	1.38	1.55	1.40
LG&E Paddy's Run, Carbide Lime	12[a]	1.23	1.27	1.48	1.31

[a] Includes fly ash and other nonsulfur solids.

Although drained sludge usually attains a bulk density in laboratory tests only slightly higher than settled sludge, the Shawnee lime sludge without fly ash, to which fly ash was subsequently added, attained a bulk density in the laboratory close to that of filtered sludge. When fly ash was admixed to the sludge, it had not developed the intimacy of mixing as when the fly ash passes through the scrubber. Consequently, the fly ash separated and settled during draining to the bottom of the column and served thereafter as a dewatering aid to produce high density.

4.3.2 Coefficient of Permeability

The physical parameter that most significantly affects the pollution potential of a sludge is the permeability of the sludge to rain water since this parameter governs the amount of leaching water passing through the sludge. Disposal techniques were developed that can minimize the recharge of rainwater to subsoils, but in all cases the permeability coefficient defines the maximum limit to the amount of liquid that can pass through the sludge.

The coefficient of permeability was measured on untreated sludges and sludge chemically treated by several processors. Permeation columns were constructed as described in Section 6.5 and Refs. 1 and 2, simulating various methods by which sludge may be disposed of, e.g., as poured; as cured; and as cured, fractured, and compacted. The rate of water passage through the columns was measured with time and as a function of the hydraulic head. In some cases, packed sludge columns were compacted or consolidated to greater particle packing densities, and the measurements were then repeated. The measured permeability coefficients are plotted as a function of volume fraction of solids in Figure 1.

The results of these measurements show that the permeability coefficients of all the untreated sludges in the condition expected in a disposed site are approximately 1×10^{-4} cm/sec (Figure 1). These results also show that for any specific sludge, there appeared the expected relationship of decreasing permeability with decreasing void volume. Additionally, there is a predominant correlation with particle size and particle packing fraction, which determines the permeability behavior of most FGD sludges. Coarser particles reach higher values of solids fraction and higher permeabilities; finer particles tend not to pack as well and have lower permeabilities. Fly-ash-containing sludges with bimodal particle distribution tend to have lower permeabilities than expected from particle size relationships. When untreated sludge is consolidated to represent the base of a 30- to 40-ft deep disposal basin, the permeability coefficient decreases to about 10^{-5} cm/sec. Table 5 shows permeability coefficients of sludges compacted under pressures of 30 and 100 psi. These values range from 10^{-4} and 10^{-5} cm/sec, or approximately one order of magnitude lower than noncompacted sludges.

Chemically treated sludges are plotted in Figure 1, and it is seen that the permeability coefficients of these materials vary considerably, depending on the treatment process and the condition of the test sample.

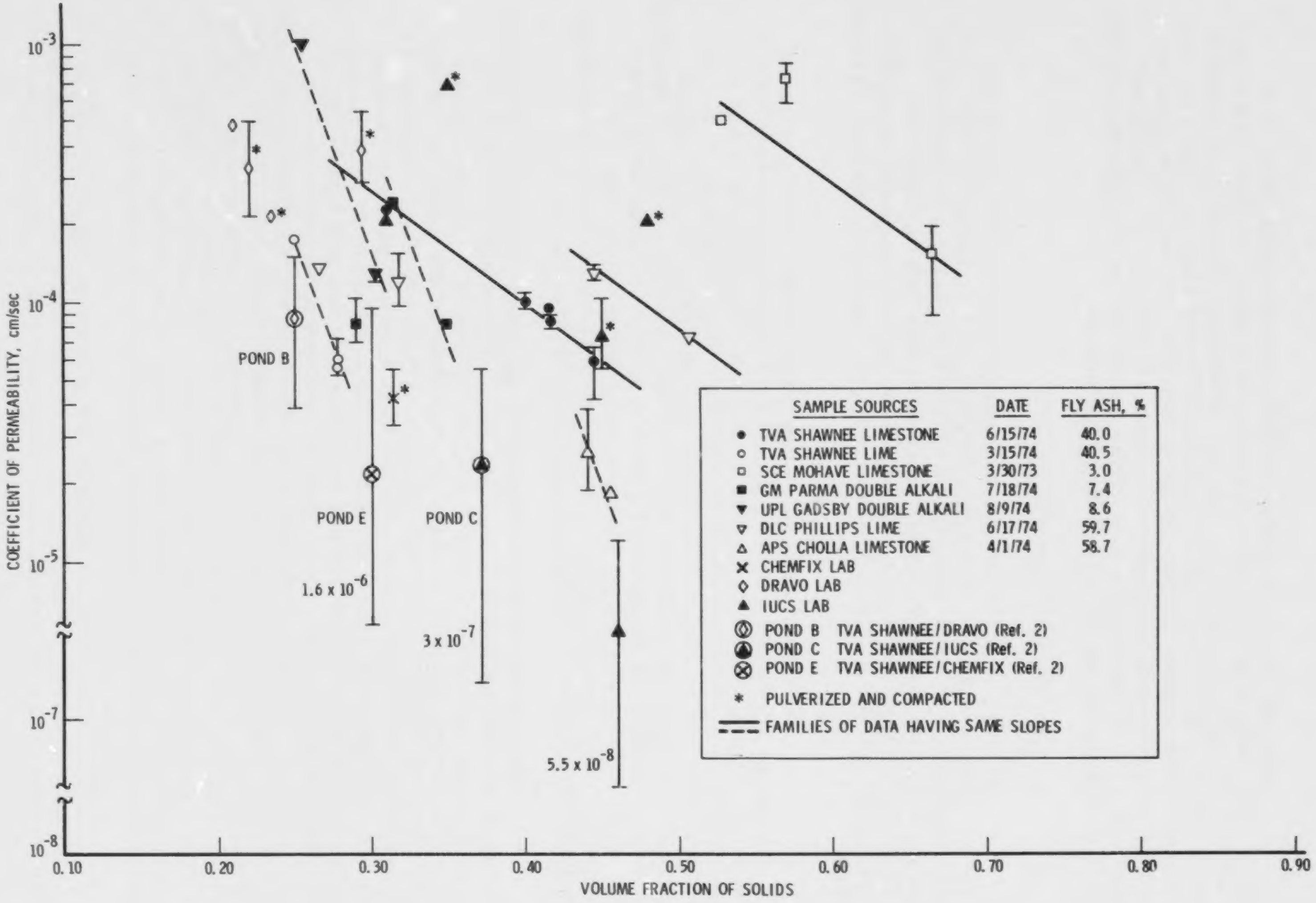

Figure 1. Permeability of chemically treated and untreated sludges

TABLE 5. PERMEABILITY COEFFICIENTS OF COMPACTED UNTREATED SLUDGE

Sludge Source	Sampling Date	Fractional Solids Volume	Permeability Coefficient cm/sec.	Consolidation Pressure (psi)
TVA Shawnee Lime (6% Fly Ash)	9/08/76	0.35	8.9×10^{-6}	100
		0.33	1.9×10^{-5}	30
TVA Shawnee Lime	9/08/76	0.47	7.3×10^{-6}	100
		0.42	1.1×10^{-5}	30
		0.41	1.4×10^{-5}	30
LG& E Paddy's Run (12% Fly Ash)		0.25	8.4×10^{-6}	100
		0.21	3.4×10^{-5}	30
GPC Scholz (Without Fly Ash)	6/20/76	0.37	1.4×10^{-4}	100
		0.34	4.4×10^{-4}	30
GPC Scholz (30% Fly Ash)	6/27/76	0.36	4.8×10^{-5}	100
		0.34	8.3×10^{-5}	30

For example, in some of these cases, measurements were conducted on treated sludges that were pulverized in order to pack the permeation column. In this condition, the columns represented material that had been placed and cured, then subsequently fractured and relocated. This method of disposal has been practiced operationally and represents a state-of-the-art technique.

Alternatively, some treated sludges were measured in a solid condition that precluded fracturing at any time. The values of permeability measurements were as low as 10^{-7} to 10^{-8} cm/sec. However, permeability measurements of these sludges, treated under field conditions (Ref. 4), have shown that the permeabilities can be expected in the range of 10^{-5} to 10^{-7} cm/sec.

4.3.3 Viscosity

The viscosity of FGD waste slurries is a direct measure of its pumpability. Thus, it affects handling procedures, transporting, and waste disposal methods. Moreover, basic system design considerations are affected by the relative ease of pumping the waste to desired locations. FGD wastes contain finely divided particulate matter suspended in a water system. This particulate matter tends to range from colloidal size to about 100 μm and consists of three major phases having markedly different morphologies. It is both the particle size distributions and phase morphologies that are believed to influence the viscosity of the sludges. Viscosity measurements were performed on sludges at varying water contents at ambient temperatures, with a commercial viscometer having a measuring range from 3 to 150 poise. Measurement procedures are described in Section 6.4.1.

The results of the viscosity tests, presented in Figure 2 for 13 sludge samples, show that easily pumpable mixtures (<20 poise) range from a high solids content of 70 percent to a low solids content of 32 percent. In addition to the position of each viscosity curve on the graph, these results further show that each viscosity curve can be separated into two rather distinct slopes.

These data indicate that particle size and particle shape, particularly the platy sulfite particles, are primarily responsible for the nature of sludge. Also, these data clearly suggest that fly ash increases fluidity of a sludge and that high pH may increase its viscosity. Whereas particle shape, size, and distribution each appear to influence viscosity behavior, the precise relationship of these parameters is not clear from these limited data.

4.3.4 Compaction

The compaction capability of FGD sludges was investigated to determine whether an economic asset might be gained by providing a means of increasing the mass of waste disposed of within a specified volume.

CURVE	SLUDGE	FLY ASH, %	DATE
1	GM PARMA DOUBLE ALKALI	7.4	7/18/74
2	UPL GADSBY DOUBLE ALKALI	8.6	8/9/74
3	TVA SHAWNEE LIME	40.5	3/19/74
4	DLC PHILLIPS LIME	59.7	6/17/74
5	TVA SHAWNEE LIMESTONE	20.1	2/1/73
6	TVA SHAWNEE LIMESTONE	40.1	6/15/74
7	TVA SHAWNEE LIMESTONE	40.9	7/11/73
8	LG&E PADDY'S RUN CARBIDE LIME	12.4	7/76
9	TVA SHAWNEE LIME	<1.0	9/8/76
10	TVA SHAWNEE LIMESTONE	<1.0	9/28/76
11	GPC SCHOLZ SODA ASH DOUBLE ALKALI	<1.0	6/20/76
12	GPS SCHOLZ SODA ASH DOUBLE ALKALI	30.0	6/27/76
13	TVA SHAWNEE LIME	40.0	9/8/76

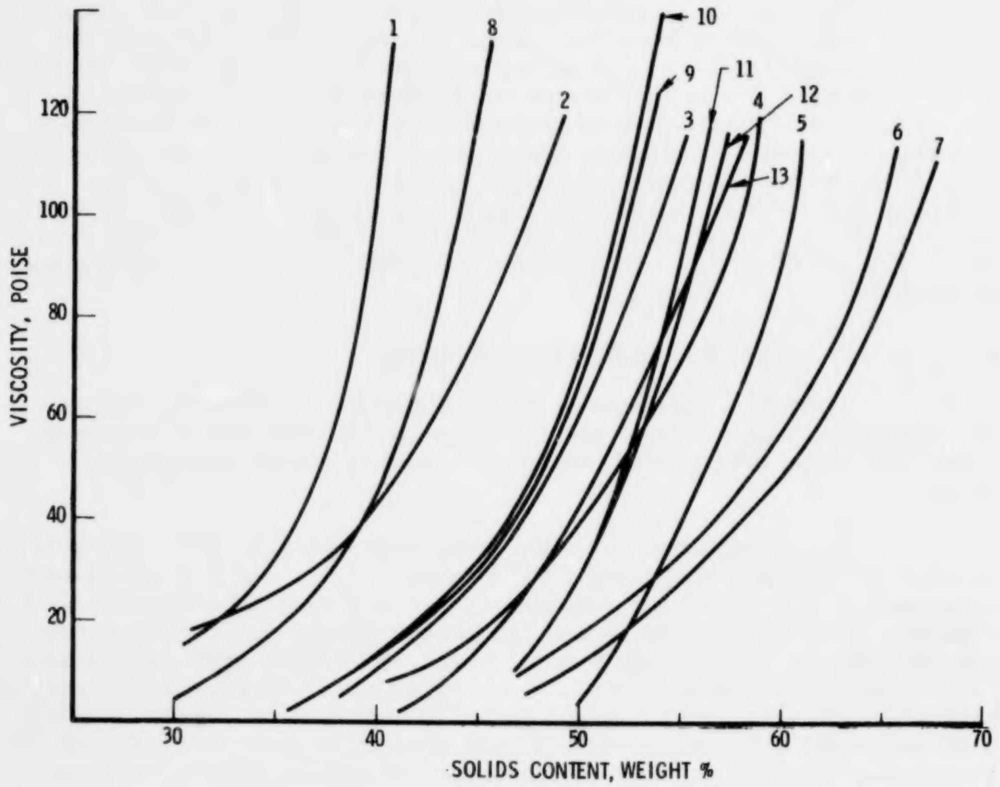

Figure 2. Viscosity of FGD sludges

Moreover, if compacted sludge behaves like fly ash, significantly reduced permeabilities and increased strength could be expected which may increase the environmental acceptability of the sludge.

The compactability of a sludge is dependent upon particles being rearranged under an applied force by sliding past each other. The process is enhanced by the presence of some pore water, which acts as a lubricant, but air voids into which the particles can move must also exist. The particle size distribution and crystalline morphology are the two most important parameters influencing the compactability of FGD sludges. The same laboratory compaction test was performed on each of the six FGD sludges at nominally 100 psi. Samples were loaded into pellet dies for the tests, and the change in sample heights was noted. There was no excess water in these samples; therefore, no water escaped during the tests. While constrained by the die, the samples deflected as much as 15 percent under the load; however, when removed from the die, the actual permanent compaction ranged between 1 and 4 percent, as shown in Figure 3. In contrast, related studies on fly ash have shown compaction of from 7 to 20 percent (Ref. 7).

The lack of compaction of laboratory tests of FGD sludges is explained by the crystal structure of the calcium sulfite platelets and the interwoven lath-like structure of the calcium sulfate crystals. In many cases, the presence of water in the pores increased the deflection under load but contributed little to the permanent deformation. The absence of significant permanent deformation resulted in no measurable increase in strength, with limited decrease in permeability to water percolation. These tests suggest that, while some benefit may be gained by mechanical compaction, it is not likely to be a cost-effective operation in untreated sludge disposal. The benefit would result from the compaction of the sludge under its own weight.

4.3.5 Unconfined Compressive Strength

Strength measured in an unconfined condition was compared with unconfined strength data of soils. These tests provided a means of estimating the suitability of FGD waste for landfill and structural fill situations.

Unconfined compression tests were conducted by standard test methods for treated and untreated FGD wastes. The results of these tests are summarized in Table 6 for samples tested in a dry (no free water), a damp (partial pore water), and a wet (as placed operationally) condition. The results indicate that, on an overall basis, untreated FGD wastes in a damp condition (~8 percent water) are stronger than samples that are dried of all water, as is the case for most soils. Nevertheless, these data indicate that untreated sludges having a solids content of approximately 85 percent or greater have unconfined compressive strengths similar to those of natural soils.

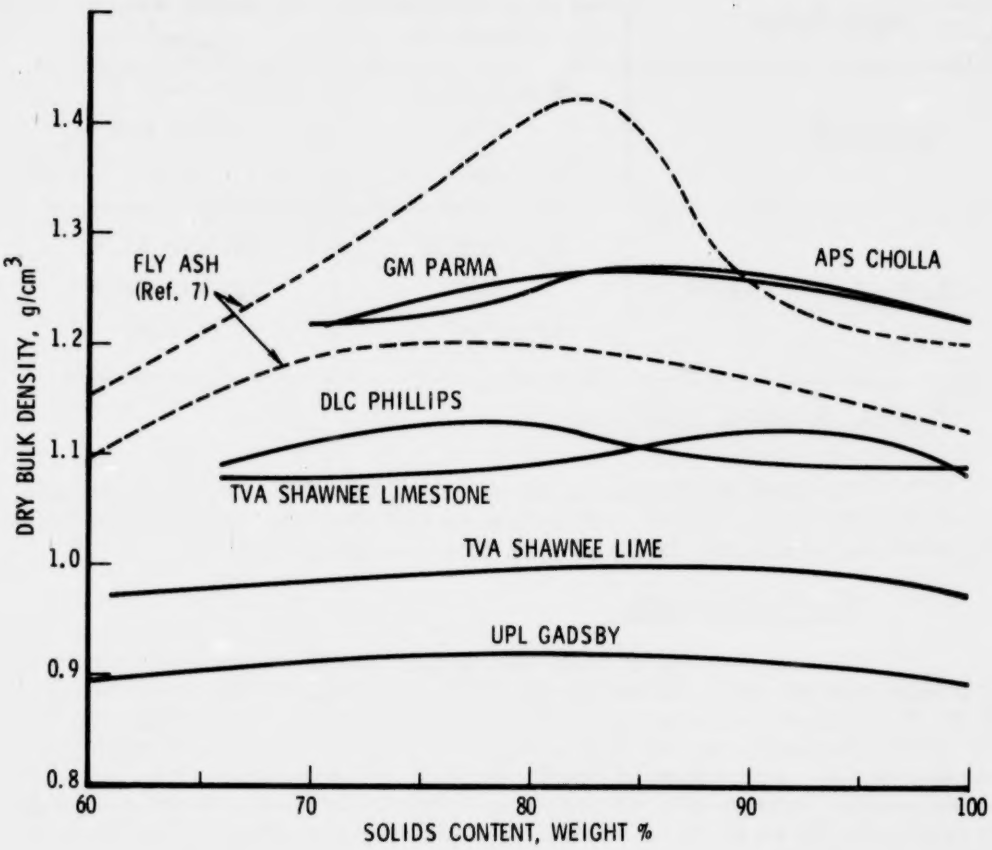

Figure 3. Dry bulk density as a function of solids content after removal of compaction loading

TABLE 6. UNCONFINED COMPRESSIVE STRENGTH TEST RESULTS SUMMARY

FGD Waste	Range of Moisture Content, %	Strength Range, ton/ft^2
Untreated	5.6 to 14.4	2.4 to 0.9
	0.0	1.5 to 0.6
	30[a]	0.0
Chemically Treated	2.4 to 5.6	48.5 to 25.4
	0.0	52.3 to 22.3
	35 to 60[a]	39 to 1.8

[a] Typical in-place conditions

Treated FGD wastes have strengths that are capable of structural landfill applications. The data do not show an appreciable difference between the strengths in the dry or wet conditions.

4.3.6 Bearing Strength

Measurements of load-bearing strength (confined) as a function of solids content were made for 10 different sludges and are plotted in Figure 4. For these samples, it is shown that each may be dewatered to a critical value of solids content above which the load-bearing strength increases steeply. The value of solids content at which this critical value is reached varies appreciably between samples. This occurs over a range of approximately 50 to 80 percent solids content, depending on the source and nature of each sludge. Of particular importance is the effect of fly ash on bearing strength, as shown for the TVA Shawnee lime and limestone samples. For both of these samples, the presence of fly ash (40 wt%) at a given solids content produced a much lower bearing strength than the sample without fly ash. The same trend holds for the Gulf Sholtz samples with and without fly ash, except that the difference in bearing strength for the two samples is not as widely separated as it is for the Shawnee samples.

The results of these tests show that untreated sludges can be dewatered such that the sludge will exhibit structural qualities and that the presence of fly ash tends to reduce the strength. Although the degree to which any sludge must be dewatered to exhibit structural qualities can be estimated from the curves of Figure 4 by comparing the nature of the sludge to those shown in the figure, its true load-bearing characteristics should be determined through experimental analysis. (It should be noted that these

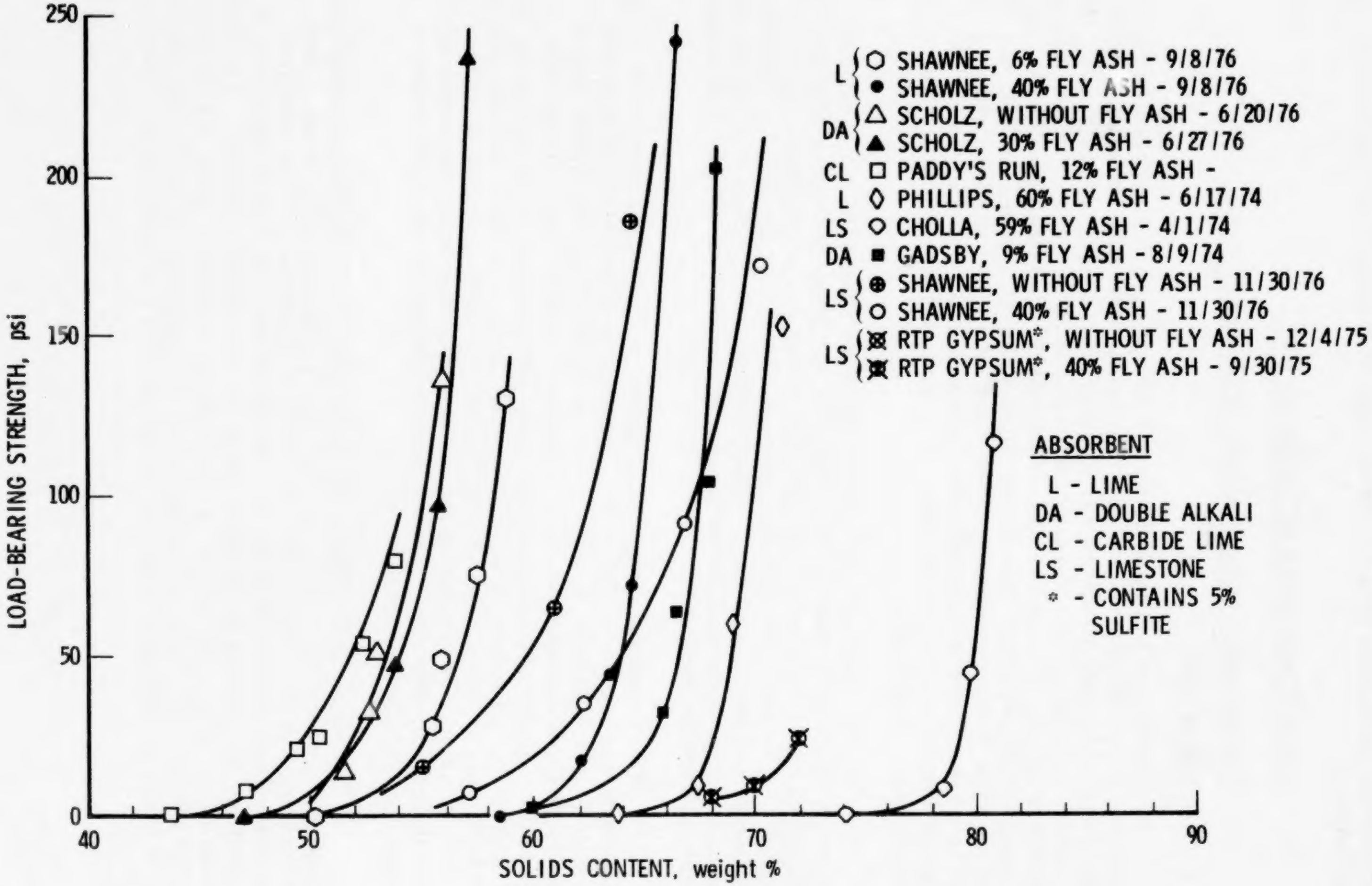

Figure 4. Load-bearing strength as a function of moisture, fly ash content, and sludge origin

materials lose their strength when rewetted and must be dewatered again by such methods as underdraining or air drying to regain their structural characteristics.)

4.4 CHEMICAL CHARACTERIZATION

4.4.1 Constituent Concentrations in Sludge Liquids and Solids

Chemical analyses from all sampling points within lime, limestone, and double alkali scrubber waste streams are summarized in Table 3, where the range of concentrations for each chemical species is given. These ranges result from an array of test conditions including some which are not representative of current technology or standard operating conditions, e.g., sample liquor obtained from unwashed filter cake of a double alkali scrubber. (For a more representative listing, see Table 2.) The distribution of trace elements in system liquors tends to lie between 0.01 and 1 mg/ℓ for all elements except mercury, which has a concentration distribution about 1/10th that of other trace elements.

Major chemical species concentrations in liquors depend strongly on the scrubber system parameters and tend to have a TDS content of about 10,000 mg/ℓ except during startup and in certain cases, such as with double alkali. The chloride concentration in the liquor depends primarily on the chlorine content of the coal. Major chemical species content in the solids also depends upon system parameters, primarily oxidation conditions and fly ash collection methods.

The crystalline phases present in the solids portion of each FGD waste are presented in Table 7. These data show that gypsum and calcium sulfite hemihydrate are the principal sulfur products and that a broad range of fly ash contents (3 to 60 percent in this study) might be expected from a survey which includes both Eastern and Western coal, with either separate or simultaneous fly ash collection. Several soluble phases were present as a consequence of salt formation during drying of occluded water. The presence of limestone in all samples was a consequence of both unreacted limestone absorbent and carbonate formation by adsorption of carbon dioxide from the atmosphere.

The source of chemical pollutants in FGD sludges originates from process ingredients: coal, combustion products, absorbents, and process makeup water. The chemical characterization of FGD sludges included analytical measurements of both the solid and liquid fractions of sludge samples at various positions along the scrubber circuits. Process ingredients from which the chemical pollutants originate were also analyzed in order to provide an understanding of the relationship between the source and fate of these potential pollutants within the FGD scrubbing processes.

TABLE 7. PHASE COMPOSITION OF FGD WASTE SOLIDS IN WEIGHT PERCENT

ATOMIC FORMULA	TVA SHAWNEE LIMESTONE, 2/1/73	TVA SHAWNEE LIMESTONE, 7/12/73	TVA SHAWNEE LIMESTONE, 6/15/74	TVA SHAWNEE LIME, 3/19/74	SCE MOHAVE LIMESTONE, 3/30/73	GM PARMA DOUBLE ALKALI, 7/17/74	APS CHOLLA LIMESTONE, 4/1/74	DLC PHILLIPS LIME, 6/17/74	UPL GADSBY DOUBLE ALKALI, 8/9/74	TVA SHAWNEE LIME, 9/8/76	LG&E PADDY'S RUN, LIME 7/76	GULF-SCHOLZ DOUBLE ALKALI, 6/20/76
$CaSO_4 \cdot 2H_2O$	21.9	15.4	31.2	6.3	84.6	48.3	17.3	19.0	63.8	19.4	15.1	94.5
$CaSO_3 \cdot 1/2H_2O$	18.5	21.4	21.8	48.8	8.0	12.9	10.8	12.9	0.2	69.2	37.4	15.3
$CaSO_4 \cdot 1/2H_2O$						19.2						
$CaCO_3$	38.7	20.2	4.5	2.5	6.3	7.7	2.5	0.2	10.8	10.3	29.5[a]	10.1
$MgSO_4 \cdot 6H_2O$	4.6	3.7	1.9	1.9								
$Na_2SO_4 \cdot 7H_2O$						6.9					7.8	
NaCl					1.5							
$CaSO_4$[b]									17.7			
FLY ASH	20.1	40.9	40.1	40.5	3.0	7.4	58.7	59.7	8.6	<1.0	12.4[a]	<1.0
OTHER							10.7[c]	8.2[c]			3.5[d]	
TOTAL	103.8	101.6	99.5	100.0	103.4	102.4	100.0	100.0	101.1	99.9	105.7	68.1

[a] The carbide lime used as absorbent is an acetylene manufacturing plant waste by-product and is reported to contain 2-2 1/2 percent silica and 3-8 percent $CaCO_3$

[b] Phase not explicitly measured; presence deduced from x-ray study

[c] Soluble salt, phase not determined; quantity by difference

[d] Carbon

4.4.2 Generation of Trace Metals in FGD Wastes

Chemical analyses of FGD sludges identified trace metals in the liquid fractions of the sludges (Table 3). The specific analyses were plotted against the analyses for coal (corrected for other process ingredients). A relationship for solids is shown in Figure 5 and for liquids, in Figure 6. This relationship shows the direct relationship between the trace metals in sludge and those in coal. In general, these data indicate that approximately one percent of the trace metals in the sludge is distributed in the liquid fraction.

The correlation that exists between the trace metal content in coal and the trace metal content in fly ash further suggests that fly ash is the principal source of these trace metals in the sludge. Furthermore, when the trace metal content of the liquor of a sludge containing no fly ash is compared with the liquor of sludge with fly ash, it is seen that fly ash causes the concentration levels to be as much as 10 times greater than those found in sludge liquors without fly ash. Also, in evaluating the data, it was found that the data points for sludge with high fly ash content tend to be on the high side of the bandwidth of Figures 5 and 6, and data points for low fly ash sludge, on the low side of the data bands.

Since the direct relationship between trace elements in sludge and in coal is clearly indicated, Western coal, having typically lower concentrations of arsenic, cadmium, mercury, and zinc than Eastern coal, is expected to produce sludges having lower concentrations of these metals. This behavior was found as expected.

4.4.3 Process Variables

An evaluation was made of the trace metal content in the system liquor at various positions in the scrubber process. Chemical analyses indicated that the system liquor pH increased and trace metal content showed a slight decrease en route from the scrubber to the disposal site. The results for trace metals may be interpreted as a response to system pH or a response to the changes taking place in the concentration of major chemical species. The in-process analyses showed, for the major species, that a rapid oxidation of sulfite ion and the precipitation of calcium sulfate also takes place en route to the disposal site. The trace metal content in the liquor may decrease by precipitation in response to decreasing ionic strength, by coprecipitation resulting from the scavenging action of the calcium sulfate, by adsorption onto newly created crystal surfaces of the calcium sulfate phase, or by pH changes previously discussed.

An evaluation of all chemical analyses of trace metals in the liquor was made as a function of both pH and ionic strength. No correlation was found for any element when chemical data from all systems were simultaneously compared, and it must be concluded that neither pH nor ionic strength are primarily variables. However, when chemical data were compared within a single system, a pH correlation was found. Thus, it is

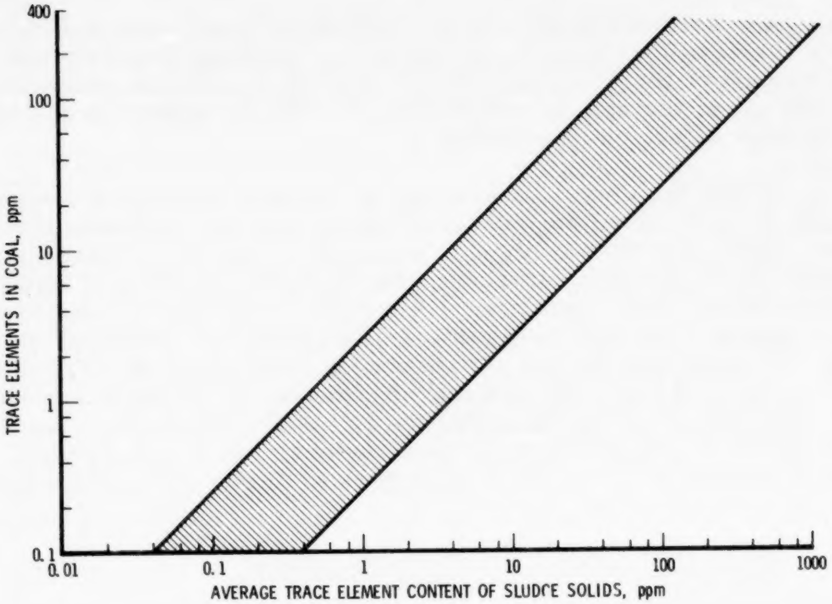

Figure 5. Relationship between trace element content in coal and sludge solids

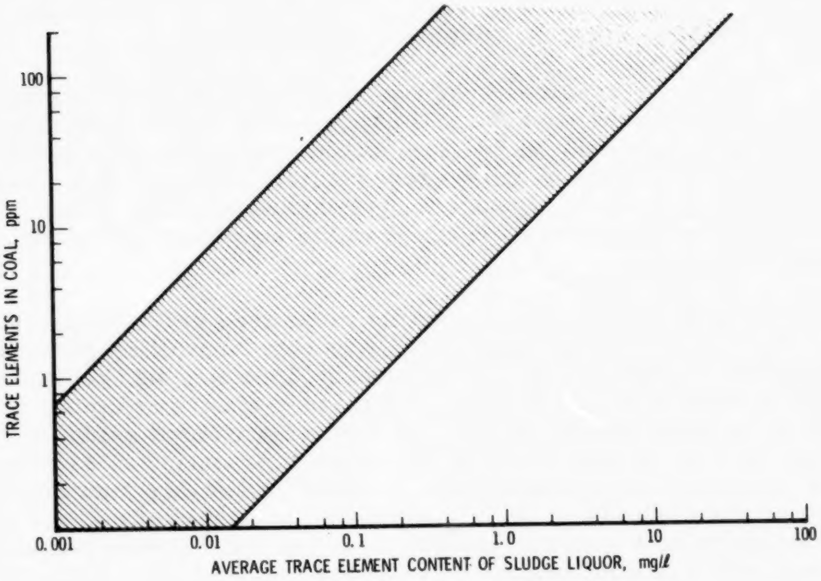

Figure 6. Relationship between trace element content in coal and sludge liquor

concluded that the primary source of trace metals is the coal and that these metals enter the scrubber system primarily by leaching from fly ash in the scrubber. The pH of the scrubber affects the trace element content in the liquor, but the pH of the system downstream of the scrubber is shown to have only a minor effect on this value.

When the chemical species in system liquor are evaluated over a period of time, the data indicate that all species increase from startup. The calcium sulfate saturation level is established quickly in most systems (although some don't operate saturated with respect to $CaSO_4 \cdot 2H_2O$) as is the concentration of trace elements. Chloride ion concentrations appear to build up at a slower rate and continue to build up until a steady state is established. As the chloride ion concentration increases, it effects an attendant increase in ionic strength that increases the calcium sulfate equilibrium levels. Trace metal contents do not reflect these changes, either from a lack of analytical sensitivity at very low concentration, lack of accuracy of analytical data, or from a lack of response to changes in major species concentrations.

4.5 CHEMICAL SOLUBILITY ANALYSES

A comparison of experimental scrubber liquor compositions with compositions calculated from the assumption of equilibrium solubility was made for each analysis by use of two computer programs. One program was specifically designed to predict maximum concentrations of trace chemical species as a function of the concentration of major species from empirical solubility data. The other program was designed to predict major species concentrations in a liquor from thermodynamic data, only, and not from the trace chemical species concentrations.

When the results of the two programs were compared for major species, it appeared that the two programs were in virtual agreement with respect to the saturation of calcium sulfate in every analysis and saturation of calcium sulfite in only a few selected cases. Moreover, the agreement between the two independent approaches relative to the experimental data provides supportive evidence to the accuracy of the experimental measurements.

For the nine trace elements measured extensively, there was no evidence that trace element saturation was the controlling parameter for the trace element concentration in the liquor. This finding is consistent with the finding of an absence of trace metal response to the most changes in major chemical species and that trace elements exceed saturation limits by several orders of magnitude. Further experimentation is required to resolve this anomaly. It is postulated, however, that this anomaly is a consequence of the analysis of ultrafine particulates (primarily fly ash) that pass through filters into the analytical solutions. If this postulation is correct, the measured concentrations of trace metals in the anomolous cases would represent condensed phases and not soluble phases, and the impact on the potential environmental hazard is greatly diminished.

4.6 ENVIRONMENTAL ACCEPTANCE OF FGD WASTE

An evaluation of the environmental impact of FGD waste was made as a consequence of the alternative routes of pollution to the environment and the methods by which the wastes may be disposed. The accessibility of pollutants to the environment can be minimized by (1) decreasing the permeability of the wastes to reduce the seepage of water, (2) reducing the leachability of the wastes through a reduction of the solubility of the material, and (3) managing seepage and runoff to limit the excess of waste constituents to groundwaters or surface waters. Disposal concepts include (1) chemical treatment of waste to effect alteration of its permeability and leachability properties, (2) total impoundment of untreated or treated wastes to isolate them from the environment, and (3) several methods of impounding untreated, dewatered wastes such that seepage and runoff are minimized. Some of these concepts produce a structurally stable material which makes site reclamation possible. The assessment of these methods shows that although intrinsic pollution prevention of each method is different from the other, the protection of the environment is best assured only through the implementation of appropriate disposal site management techniques.

4.6.1 Pollutant Access to the Environment

An evaluation of the chemical pollutant potential to the environment by vaporization has shown that this hazard is essentially nonexistent. Pollution by wind-whipped spray or runoff is determined by the quality of the supernate and can be as contaminated as system liquor or as benign as rainwater. In the case of runoff, suspended solids may be a more critical pollutant than dissolved solids, especially for untreated waste.

During the course of this study, no wind-blown emissions or effects thereof were noted at air-dried ponds, either untreated or chemically treated. It is assumed, however, that in arid areas or in humid areas during drought conditions, fugitive emissions could be a problem and that such a site would be managed similarly to an earth landfill; i.e., the surface material could be moistened or the site could be covered and vegetated.

By far the most persistent pollution potential is by water percolation through the sludge and subsoil into the subterranean water table. The severity of the pollution is dependent upon both the quantity and quality of the leachate from the disposal sites. Leachate quality was determined by laboratory experimentation by leaching column tests. Results from these tests show that the concentration of all chemical species decreases continually in the leachate, initially at a high rate. After the displacement of 3 to 5 pore volumes, however, the rate of decrease is typically very low, or the concentration becomes constant. The initial high rate of decrease is believed to be a consequence of a flushing mechanism; the constant or low-rate segment appears to be the consequence of the solubility of crystalline phases.

Chemical treatment of a waste by fixation processing produces a leachate with concentration values of major species nominally one-half of untreated sludge initially. Highly soluble chemical species like sodium and chloride ions are removed effectively from the system in the initial pore flushing, and after approximately five pore volume displacements (PVD), the TDS consist primarily of calcium and sulfate ions. Leachate of untreated sludge follows a similar pattern, except the maximum concentration levels are approximately the same as those of the input liquor (Ref. 4).

Both treated and untreated sludge leachates reach gypsum saturation concentrations after approximately five PVD.

Chemical treatment did not reveal a discernible difference from untreated material for trace metals. In most cases, all trace metal content in the leachate dropped below detection levels after the initial flushing. In the remaining cases, only lead, zinc, and selenium were found for both treated and untreated sludges to persist at concentration levels significantly above the background.

4.6.2 Alternative Disposal Techniques

The methods by which FGD waste may be disposed of will be determined by the environmental acceptability of the waste and the cost of waste disposal. In addition, methods already used in fly ash disposal or in the disposal of other industrial wastes may be used in preference to new or untried techniques. Thus, sludge sluicing to a pond is considered a viable method but may require a pond liner in the event that environmental pollution may otherwise occur. The physical properties of ponded sludge are such that structural stability does not develop and subsequent land use is obviated. Upon retirement of the pond, supernate can be withdrawn, the sludge may possibly be air dried and an overburden can then be placed on the site. The additional cost and time required for this type of reclamation even if possible may increase total costs such that ponding is not cost effective relative to other methods. An alternative to ponding is the technique whereby the sludge is sluiced to the disposal basin. Instead of supernate liquor collection, the disposal basin is underdrained, and the excess liquor is returned to the scrubber. Dewatering by underdrainage enhances structural properties such that land reclamation can be implemented within a few days.

An alternative method for disposal of untreated waste uses a filter or centrifuge to provide a material that can be transported and placed by truck transfer. While transportation costs for this method are intrinsically high, the method may offer advantages that offset trucking costs. Particular attention to disposal site management especially as related to structural stability may be necessary in this method.

Chemical treatment of FGD wastes provides an additional assurance of environmental acceptance, but this material must be placed in a disposal site in a manner consistent with sound disposal practices. This method is the most expensive among the various disposal alternatives but may be necessary in certain cases where structural stability of environmental protection might otherwise be compromised.

In the case of chemically treated waste, it is possible to dispose of the waste in a manner resembling ponding, similar to the Pennsylvania Power Company's Bruce Mansfield Station disposal operation. Monitoring of local streams is necessary because of the potential seepage of leachate caused by the constant hydraulic head of the impounded water.

4.6.3 Environmental Benefits of Chemical Treatment

Chemical treatment has been found to have major benefits which effectively minimize (and possibly, in some cases, virtually eliminate) the release of leached sludge constituents to the subsoil through (1) the decreased permeability of the treated material, and (2) the amenability of the treated material to compaction and contouring during placement so that standing water does not occur on the disposal site. The prevention of standing water avoids having a hydraulic head on the site; therefore, seepage through the pores does not occur as a result of hydraulic pressure. This is accomplished by managing the site so that a major portion of the rainfall on such a site runs off and is collected in a peripheral ditch which directs the water to a settling pond, from which decanted liquor is disposed of in an adjacent stream, if acceptable, or returned to the power plant water reuse system.

Various examples illustrating the effects of sludge treatment, effects of different subsoils, and management of the site for different rainfall recharge rates are presented. The relative amounts of sludge constituents (TDS) released at the sludge base for different modes of disposal were calculated (Table 8 and Figure 7). The figure illustrates the benefit of chemical treatment, particularly when disposal is on a highly permeable soil which otherwise would not be supportive if ponded.

This analysis is based on correlations of laboratory results and Shawnee field condition data reported in Reference 4. All the cases are indexed to an untreated slurry pond, Case 1, in which the soil permeability coefficient is 10^{-5} cm/sec.

In assessing the effectiveness of chemical treatment, tests to determine permeability of chemically treated sludges were performed on cores extracted from the Shawnee field evaluation site. Constant-head permeability tests were run on (1) pulverized samples, and (2) samples with and without visible cracks. Uncracked samples of one material had coefficients of permeability of about 10^{-7} cm/sec; the pulverized and the cracked samples had coefficients of approximately 10^{-5} cm/sec. Therefore, the effective coefficient of the treated material could be expected to be between 10^{-5} and 10^{-7} cm/sec. In a conservative case (using a coefficient of 10^{-5}),

TABLE 8. BENEFITS OF CHEMICAL TREATMENT: CASE STUDIES FOR COMPARISON OF MASS RELEASE OF SLUDGE CONSTITUENTS FOR VARIOUS DISPOSAL ALTERNATIVES

Case	Disposal Method[a]	Surface Water	Sludge Condition[b]	Sludge Permeability, cm/sec
1	Ponded slurry	Constant supernate[c]	Untreated	10^{-4}
2	Ponded slurry	Constant supernate	Chemically treated	10^{-5}
3	Ponded cake	10-in/yr recharge[d]	Untreated	10^{-4}
4	Dewatered and ponded	10-in/yr recharge[d]	Chemically treated	10^{-5}
5	Landfill	1-in/yr recharge[e]	Chemically treated	10^{-5}

[a] Fill period = 5 yr; depth = 30 ft.

[b] Porosity (void volumetric fraction) = 0.67.

[c] Constant supernate assumes 1-ft depth of surface water.

[d] 10-in/yr recharge is unevaporated rainfall.

[e] 1-in/yr effective recharge resulting from seepage during runoff of rainfall.

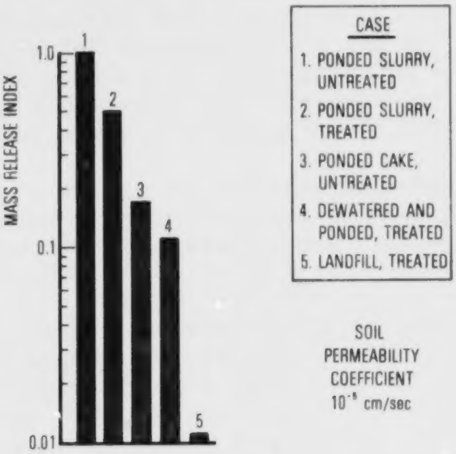

Figure 7. Comparison of mass release of sludge constituents for various disposal alternatives showing benefit of chemical treatment

an order of magnitude improvement in impermeability is realized compared to untreated sludges, which typically have a coefficient of about 10^{-4}.

The systematic reduction of standing water is illustrated in Cases 3 through 5, wherein the recharge rate is reduced compared to a ponded slurry. If only unevaporated rainfall is allowed to recharge, the mass release into the subsoil is reduced by a factor of about 5 (Case 3 versus 1, and Case 4 versus 2).

The significance of eliminating standing water by runoff is shown. If it is assumed that 10 percent of the net rainfall is recharged, then a one order of magnitude reduction is achieved relative to a dewatered and ponded treated waste (Case 5 versus 4), and two to three orders of improvement depending on soil permeability when comparing the mass seepage from a chemically treated site to that of a ponded untreated site (Case 5 versus 1). In addition, compacting the treated materials during the site filling may reduce crack formation so that an effective coefficient of permeability better than 10^{-5} cm/sec may be realized.

Case 2 (Figure 7) considers chemically treated sludge disposal in such a manner that a hydraulic head exists on the site at all times. The mass release for such a case is approximately 1/2 to 1/20 of that from an untreated slurry pond, depending on subsoil permeability. Sites of this type may seep to an adjacent stream or water table, which may reduce the concentration of constituents because of mixing. Historical data regarding the stream and water table characteristics and quality, as well as monitoring, may be mandatory for sites of this type to assure environmental acceptability.

4.6.4 Gypsum

4.6.4.1 Physical Properties

Measurements were made on samples obtained from the EPA Research Triangle Park (RTP) forced oxidation pilot unit. These measurements were of permeability coefficient, void fraction, water retention, density, unconfined compressive strength of fly-ash-free first-stage scrubber (gypsum), second-stage solids (calcium sulfite), and filter solids (gypsum mixed with 5 to 10 percent calcium sulfite). The effects of fly ash on the properties of the various materials were also determined:

a. Permeability coefficients for the predominantly gypsum and predominantly calcium sulfite were virtually the same, approximately 1×10^{-4} cm/sec.

b. The pore volume fractions of gypsum solids without and with fly ash range from 0.55 to 0.5, respectively. Wet bulk densities were approximately 1.3 and 1.4 g/cm^3, respectively.

c. The first-stage solids (gypsum) showed substantially higher unconfined compressive strength (60 psi) than the second-stage solids (calcium sulfite). When the gypsum contained 5 to 10 percent calcium sulfite, the unconfined strength was approximately that of the sulfite (15 psi). The presence of fly ash did not appreciably affect the unconfined compressive strength.

d. Gypsum filtered to approximately 85 percent solids.

Field evaluations of gypsum disposal are being conducted at the Shawnee disposal evaluation site. When completed, results will be discussed in a separate report on the Shawnee work.

4.6.4.2 Leaching Characteristics

The leachate from the filtered solids and solids from first-stage slurries after 2 to 3 PVD of water had passed through the samples was saturated with calcium and sulfate ions. This was typical for all samples except for leachates from the two second-stage slurry solids at 10 and 22 PVD, whereby the gypsum supply had been essentially depleted. At that point, these two were saturated with calcium sulfite. Thereafter, the calcium was supplied by the dissolution of hydrated calcium sulfite, although the anion found in the leachate was sulfate because of the rapid oxidation of sulfite ions.

During leaching, the soluble magnesium and calcium chlorides were washed out of the solids with the residual liquor, leaving the crystalline gypsum to saturate the leaching water. The ionic strength decreased as the chlorides were removed, thus reducing the solubility of gypsum, which leveled out at the same saturation value of about 2200 mg/ℓ.

4.6.5 Alternative Disposal Method for Untreated Wastes

The data obtained to date on the concentration of dissolved solids in the leachates of untreated sludge show that peak levels are reached which are virtually the same as those of the input sludge liquor. These concentration levels have been found to exceed drinking water criteria; therefore, some form of control is needed. In addition to the use of impermeable liners or soils, one method being investigated is the use of an underdrain system whereby the underdrained water is returned to the scrubber loop for reuse. An underdrain, vented to the atmosphere, minimizes seepage by eliminating the hydraulic head of the leachate. The gravity head of any accumulated surface water is adequate to provide for rapid removal of rainfall recharge. This technique has the potential for increasing the bearing strength of the sludge to levels useful in a landfill. This disposal operation has been investigated in laboratory tests and is currently being evaluated in the field for lime and limestone sludges and gypsum (Ref. 4). As of this writing, each has supported construction equipment, i.e., tractors and front-end loaders.

A water balance analysis (Section IX) has shown that this mode of closed-loop operation (with underdrainage water return) is possible, including the maintenance of tolerable chloride ion levels and minimum impact of fresh water makeup.

4.7 DISPOSAL COST ESTIMATES

Cost estimates for ponding and chemical treatment/landfilling have been made and reported by Aerospace on several occasions. During studies associated with the EPA Shawnee field disposal evaluation project, Aerospace cost estimates were made of chemical treatment disposal and were reported in the initial report on that study (Ref. 3). The Aerospace estimates for lined-pond costs were presented in the initial and second progress reports on sludge disposal (Refs. 1 and 2) and at the EPA flue gas desulfurization symposia (Refs. 8, 9, and 10). All estimates were updated (in a report to EPA on new source performance standards) to a July 1977 basis, and are summarized herein. A summary of these cost estimates is presented in Table 9, and a discussion of the study is given in Section X.

TABLE 9. DISPOSAL COST COMPARISON[a]

Cost Basis, Mid-1977 $	Ponding		Landfill Chemical Treatment	Gypsum
	Indigenous Clay	Liner Added		
Mills/kWh	0.55	0.80	1.05	1.10
$/ton sludge (dry)	4.90	7.25	9.70	10.30[m]
$/ton coal	1.50	2.20	2.95	3.10

Notes

a. Dollar base:	July 1977
b. Plant characteristics:	1000 MWe, 8700 Btu/kWh (0.73-lb coal/kWh)
c. Coal burned:	3.5% sulfur, 12,000 Btu/lb, 14% ash
d. Annual average operating hours:	4380 hr/yr (30-yr avg)
e. Plant and disposal site lifetime:	30 yr
f. SO_2 removal, with limestone absorbent	90%
g. Limestone utilization	80% all cases except for gypsum, which is 100%
h. Sludge generated:	4.8×10^5 short tons/yr untreated waste (dry) including ash
i. Average annual capital charges, 30-yr average:	18% of total capital investment
j. Cost of land used for disposal:	$5000/acre, all land assumed purchased initially, sludge depth, 30 ft
k. Land depreciation:	Total depreciation in 30 yr, straight line basis
l. Disposal site:	Within one mile of plant
m. Cost of forced oxidation and disposal of gypsum shown as cost/ton of equivalent quantity of nonoxidized sludge. Divide by 1.08 to convert to gypsum cost.	Includes fly ash; disposal is in a clay-lined pond

SECTION V

DISPOSAL CRITERIA

The principal objectives of this study are to evaluate and determine environmentally acceptable methods for disposal of FGD sludges, emphasizing landfilling and ponding. Throughout the study, in the absence of appropriate federal or other criteria relating to the disposal of these materials, drinking water criteria have been used as a basis for establishing requirements for disposal. Because the trace element and salt content of most samples analyzed exceeded the drinking water criteria, at least for some of the constituents, the approach taken in this study has been to dispose of the flue gas desulfurization (FGD) sludges such that no direct discharge to any water supply would be allowed and that any seepage or runoff would be minimized or, perhaps, totally eliminated. Various methods of disposal have been studied and evaluated in the field (Refs. 3 and 4), and are discussed in Section IX.

During the period of performance of the final phase of this study, the Resource Conservation and Recovery Act (RCRA), Public Law 94-580, was enacted (October 1976). Under the provisions of this act the U.S. Environmental Protection Agency (EPA) has been directed to provide regulations and guidance to control the disposal of hazardous and nonhazardous wastes including solid waste, which includes FGD sludges (air pollution control sludges). Under the provisions of the RCRA, the EPA is to develop a definition of hazardous wastes. Under various criteria, toxicity will undoubtedly be included and could pertain to FGD sludges. If these sludges are defined to be hazardous, the generation, transportation, and disposal would be controlled by EPA regulations as a minimum. If the sludges are determined to be nonhazardous, disposal would be controlled under the provisions of the RCRA land disposal program. EPA would produce disposal guidelines, but the responsibility for disposal would be that of the states.

At this time the "hazardous" and "nonhazardous" definitions are still being formulated, and formal nonhazardous disposal guidelines have not been promulgated. This section, therefore, discusses the environmental acceptability of FGD sludge disposal in terms of preventing or minimizing the pollution of groundwaters or surface streams, using the best practical technology available today. Criteria discussions given in the second progress report on this study (Ref. 1) are repeated as appropriate and updated to incorporate progress during the final phase.

A comparison of the chemical constituents of sludge liquors in a discharge stream with the National Interim Primary Drinking Water Regulation (NIPDWR) is given in Table 10 as a ratio of constituent concentration to water criteria. These ratios are given for the ranges of constituents from all samples analyzed (see Table 11), and for six more recent samples whose values can be seen in Section 7 for those analyzed in the final phase of this study, and in Reference 1 for previous analyses. It should be noted that the values used in this comparative analysis represent the initial release of these constituents from the base of an untreated disposal site, and that continued leaching of a given sample would result in a reduction of concentrations.

In Table 11 the ratios for concentrations in the "Range of All Samples" column show that all elements analyzed plus the total dissolved solids (TDS) and pH exceed drinking water criteria. However, in observing ratios for the 10 independent samples shown in the table it can be seen that except for selenium in two samples and cadmium in one, no trace element exceeds the criteria by a factor greater than 10. (Water criteria for barium, nitrate, and silver are 1, 10, and 0.05 mg/ℓ, respectively. Limited field evaluation leachate data show maximum concentrations for these elements to be about 5, 1, and 0.5 times the criteria, respectively.) The TDS are high for most of the samples, and the pH is excessive for two of the samples. Although trace elements are not eliminated as a matter of concern by these data, there are indications that in many cases the concentrations are quite low and that the item for concern may generally be the concentration of dissolved solids in some cases, pH, and possibly chemical oxygen demand (COD), as noted in Section 5.2.1. It is difficult at this point in consideration of potential experimental error, the depletion of the material with leaching time, cation exchange and adsorption in the soil, and dilution between the disposal site and the consumer tap to specifically quantify the degree of pollution potential from the disposal of these sludges. Because of the comparatively large concentration of dissolved solids and the identification of random values of high concentrations of trace elements, methods to dispose of these materials while preventing their access to the public water supply have been assessed. These include chemical treatment and landfilling, disposal in impermeable ponds, and disposal in basins equipped with underdrainage. These methods are discussed in the following paragraphs with regard to preventing pollution of public water supplies.

5.1 DISPOSAL ALTERNATIVES FOR FGD SLUDGES

The general categories of disposal and the considerations required for environmental control are shown in Table 12. In each case, seepage of rainwater through the waste and eventual contamination of groundwater pose an environmental concern for all disposal methods. Runoff is a potential source of environmental pollution for landfill sites because, by

TABLE 10. COMPARISON OF SLUDGE LIQUOR WITH DRINKING WATER CRITERIA

NIPDWR Drinking Water Criteria, mg/ℓ	Concentration ÷ Criteria (Nondimensional)										
	Range of All Samples	Sample[a]									
		A	B	C	D	E	F	G	H	I	J
As 0.05	< 0.8 - 2.8	0.6	0.4	2.0	0.04	0.4	1.2	2.8	0.1	0.8	0.2
Cd 0.01	0.4 - 11	5.0	1.2	0.4	--	11	1.3	--	--	5	2.5
Cr 0.05	0.22 - 5	5.0	0.8	1.8	--	0.6	0.2	--	--	--	1.1
Pb 0.05	0.2 - 6.6	0.8	3.0	4.6	<0.2	6.6	0.2	< 0.2	< 0.2	0.8	< 0.1
Hg 0.002	0.03 - 2.5	2.5	--	--	<0.1	< 0.5	< 0.001	< 0.1	< 0.1	0.1	0.03
Se 0.01	0.28 - 20	10.0	3.3	10.0	4.2	< 2	7.8	20	14	2.8	0.3
F ~2	< 0.5 - 5	--	0.5	3.3	--	1.7	1	--	--	5	< 0.5
TDS 500	6.6 - 48.5	36	6.6	30.0	13.4	18.8	20.5	28	18.4	8.4	48.5
pH (actual values)[b]	6.7 - 12.2	6.7	6.8	8.0	12.2	8.7	8.0	7.8	7.3	10.7	8.9

[a] Sample data are as follows:

Sample	Station	Absorbent	% Ash	Sampling Date
A	Mohave	Limestone	3	Mar 1973
B	Cholla	Limestone	59	Nov 1974
C	Shawnee	Limestone	40	Jun 1974
D	Shawnee	Limestone	6	Jan 1977
E	Shawnee	Lime	40	Jun 1974
F	Shawnee	Lime	6	Sep 1976
G	Shawnee	Lime	6	Oct 1976
H	Shawnee	Limestone[c]	6	Aug 1977
I	Duquesne Phillips	Lime	60	Jun 1974
J	LG&E Paddy's Run	Carbide lime	12	Jul 1976

[b] EPA-proposed secondary regulation is 6.5 to 8.5.

[c] Forced-oxidized to gypsum.

TABLE 11. RANGE OF CONCENTRATIONS OF CHEMICAL CONSTITUENTS IN FGD SLUDGE LIQUORS THROUGHOUT THE SCRUBBER LOOP[a]

Scrubber Constituents	Sludge Liquors, mg/ℓ
Aluminum	0.03 to 2.0
Arsenic	0.004 to 1.8
Beryllium	0.001 to 0.18
Cadmium	0.004 to 0.11
Calcium	10 to 2600
Chromium	0.011 to 0.5
Copper	0.002 to 0.56
Lead	0.005 to 0.52
Magnesium	0.1 to 2750
Mercury	0.00005 to 0.07
Potassium	5.9 to 760
Selenium	0.0006 to 2.7
Sodium	10.0 to 29,000
Zinc	0.001 to 0.59
Chloride	420 to 33,000
Fluoride	0.6 to 58
Sulfate	600 to 84,000
Sulfite	0.9 to 3500
TDS	2800 to 162,700
pH	4.3 to 12.7
COD	40 to 140

[a] All test conditions not necessarily standard. See Table 10 for representative list.

TABLE 12. ENVIRONMENTAL EFFECTS OF DISPOSAL ALTERNATIVES

Type of Disposal	Condition of Waste	Primary Drainage	Environmental Effect		
			Seepage	Runoff	Land Reuse
Pond	Untreated[a]	Supernate	Yes	No	No
	or chemically treated[b]	Supernate	Yes	No	Yes
Basin	Untreated[a] or conditioned[c]	Underdrainage	Yes	No	Yes
Landfill	Conditioned[c] or chemically treated[b]	Runoff	Yes	Yes	Yes

[a] Untreated waste refers to FGD sludges as emitted from primary or secondary dewatering equipment.

[b] Chemically treated sludges refer to the waste treated by one of several commercial processes that make these wastes suitable for landfill disposal.

[c] Conditioned waste refers to sludge treated by techniques other than chemical treatment and includes oxidation to gypsum and dewatering by mixing with dry fly ash or other agents that allow the material to be handled in a manner similar to that for soils.

definition, these sites are open and do not necessarily return water to the scrubber. Only in the case of ponding is it clear that the disposal site is not directly amenable to land reclamation efforts, although even in some of these cases it may be possible upon retirement to air-dry, cap, and vegetate the site.

5.2 ENVIRONMENTAL EFFECTS OF FGD WASTE DISPOSAL ALTERNATIVES

5.2.1 Rainwater Seepage

One of the difficulties in applying existing water quality standards to FGD waste waters is that they apply to the quality of the groundwater or tap water and do not directly define the quality of seepage waters from a FGD waste disposal site. Nevertheless, possible approaches, either individually or in combination to control seepage, are as follows:

a. Eliminate seepage by using impermeable liners or by collecting and recycling all seepage.

b. Account for attenuation via adsorption or cation exchange in underlying soil.

c. Force-mix seepage with groundwater for dilution.

d. Mix seepage and groundwater with connecting streams.

e. Chemically reduce solubility and/or permeability and mix with groundwater.

f. Chemically reduce solubility and/or permeability and reduce or eliminate seepage by maximizing runoff.

The selection of techniques to accommodate anticipated standards for groundwater quality as a consequence of FGD waste seepage will depend on climatological, geological, and hydrological considerations of the disposal site, as well as the quality of leachate that emits from the site. Typical concentrations of leachate from untreated sludges are given in Table 11. Reduced concentrations as a result of pore volume displacement (PVD) can be seen in Table 13, which gives data for untreated and chemically treated sludges but not necessarily those analyzed for Table 11. Nonetheless, reductions as a result of seepage are evident. The conditions represented in Table 13, however, apply only to cases where fresh sludge is not continually added to the disposal site.

Mass loading of constituents is determined for site specific conditions (Section IX), with rainfall quantities, material and soil permeability coefficients, and method of disposal being the more significant factors.

TABLE 13. CHEMICAL CONSTITUENTS IN LEACHATE FROM UNTREATED AND CHEMICALLY TREATED TVA SHAWNEE FGD WASTE AFTER 1 AND 50 PVD[a]

Chemical Constituent	Untreated Waste		Treated Waste	
	1st PVD	50th PVD	1st PVD	50th PVD
Arsenic	0.02	0.004	0.015	<0.004
Beryllium	0.01	<0.004	0.008	<0.002
Cadmium	0.015	0.002	0.02	0.002
Chromium	0.045	<0.003	0.06	0.003
Calcium	-	0.010	0.025	0.005
Lead	0.25	0.010	0.15	0.03
Mercury	0.0005	<0.00005	0.0007	0.0002
Selenium	0.055	0.006	0.040	0.008
Zinc	0.65	0.04	0.27	0.03
Chloride	2600	100	600	75
Fluoride	4.0	0.8	1.1	0.4
Sulfite	50	30	35	20
Sulfate	6500	1200	3500	450
Total Dissolved Solids	10,000	2200	6000	1000
Chemical Oxygen Demand	10	6	7	4
pH	6.6	5.5	6.8	8.0

[a] Concentrations in mg/ℓ, as appropriate.

Therefore, for example, if mixing of seepage with ground waters or surface waters is considered, the sludge mass and constituent concentrations, as well as the site specific conditions, would be necessary for determination of the environmental impact.

In Table 11, it is shown that values of COD in fresh sludge ranged between 40 and 140 mg/ℓ. Because of the rapid oxidation characteristic of sulfite sludge, the COD after 1 PVD was 10 mg/ℓ or less and after 50 PVD was 6 mg/ℓ or less. All soils are not aerobic; therefore, COD could be considered a critical parameter. The potential ecological impact of high COD values was not determined.

5.2.2 Landfill Runoff

For the landfill method of disposal, runoff is a major concern for environmental control. For those cases where runoff is allowed to inundate adjacent flatland through which it may permeate, only regulations pertaining to seepage are applicable. For other cases where runoff is directed to receiving streams, the most applicable regulations are state stream standards. Thus, where the receiving stream size is small relative to water supplied in the stream by landfill runoff, the prevention of stream contamination may be a primary environmental concern. As in the case of seepage, the method selected for the prevention of pollution is determined by the quality of runoff waters. Possible approaches for the prevention of stream contamination are as follows:

a. Collect all runoff in lined siltation ponds.

b. Cover and vegetate landfill so that runoff water quality is not contaminated by the FGD waste.

c. Force-mix runoff waters with stream waters.

d. Divert runoff to flatland where evaporation and seepage can take place.

e. Dilute landfill runoff with runoff from other sources before emitting to streams.

Selection of any of these alternatives is dependent upon site-specific considerations.

5.2.3 Land Reuse

In addition to chemical contamination prevention, environmental concern also includes the attainment of certain structural qualities if the site is to be reclaimed. In the absence of specific criteria, a conservative value of 1.8 kg/cm^2 (25 psi) minimum unconfined compressive strength was considered because it could be met on the basis of the following observations (a minimum allowable value was not determined):

a. Heavy equipment on tires carrying 45 psi and driven repeatedly onto a saturated, chemically treated pond at the TVA Shawnee field evaluation site (Refs. 3 and 4) has maintained traction and left only a mild track in the material. This material has an unconfined compressive strength of 27 psi in a wet condition.

b. All chemically treated wastes studied attained and usually exceeded this strength.

c. The standard test for unconfined compressive strength is simple and inexpensive.

Studies are continuing in the Shawnee field disposal evaluation project (Refs. 3 and 4) to relate disposal site strength to confined compressive strength criteria and to include untreated sludges that attain a degree of strength through dewatering.

5.3 SELECTION OF DISPOSAL CRITERIA

It has been demonstrated that disposal methods exist by which anticipated chemical and structural criteria can be met. Simply stated, if reclamation of the land is not required, ponding in a naturally impermeable or lined basin is adequate. If structural characteristics are required, chemical treatment of the material and placement in an impermeable basin would certainly provide adequate strength and would not allow pollution of groundwaters. Moreover, a lined siltation pond can assure environmental protection from any runoff waters. However, this solution may be overly conservative and incur costs beyond that which may be necessary.

Demonstrations, both small-scale and operational, of treated and conditioned waste landfills (without liners) are now in progress and should verify the environmental acceptability of such sites when managed to prevent the collection of water on the surface and, thereby, the elimination of hydraulic heads and subsequent seepage. Runoff is collected in a siltation pond where suspended solids settle and are periodically dredged and returned to the fixation process. One operational fixed waste disposal site allows surface water. Its environmental acceptability is partially based upon the mixing of seepage with groundwater, a nearby stream, and a connecting river. All sites are monitored for water quality.

It is apparent that each disposal site and the material placed on it have individual characteristics different from most others. These include waste material properties, weather, topography, soil characteristics, and nearby stream quality and flow characteristics. Therefore, the disposal method chosen for any site will generally be selected on site-specific conditions. Because of this, the establishment of a single criterion for all cases may be impractical.

At this time, studies are continuing in the Shawnee field disposal evaluation project, other EPA projects, and in industry to define and evaluate environmentally sound, least-cost methods of waste disposal, covering the range of ponding, dewatering and mixing with fly ash, ponding with underdrainage, conversion to gypsum and dewatering, chemical treatment, ocean disposal, and mine disposal. Data from these studies are expected to provide a base from which an appropriate disposal mode may be selected for any given site.

A detailed discussion of disposal and environmental relationships and the methodology of alternative disposal techniques is given in Section IX.

SECTION VI

PHYSICAL PROPERTIES DETERMINATION

6.1 BACKGROUND

The disposal, handling and transportation techniques applied to flue gas desulfurization (FGD) wastes are strongly dependent upon the physical behavior of these wastes and the resultant costs. The predominant physical properties that limit or restrict the applicability of most of these techniques include the degree of solids content; the crystalline phase composition; and the particle size, shape, and distribution. Experimental tests were conducted to determine the physical characteristics of the FGD wastes from power plant scrubbing facilities that supported this program. These tests were directed toward sludge usage in landfilling and land reclamation applications.

The physical parameters investigated include specific gravity, bulk density as a function of solids content, water retention for particular dewatering techniques, viscosity of slurries at various water contents, permeability as a function of volume fraction solids (converse of void fraction), and bearing capacity as a function of solids content. Additionally, crystalline structure was observed, using a scanning electron microscope (SEM), and correlations were made between these observations and the physical behavior of the respective samples.

The following subsections describe the tests conducted and results of the tests for each of the FGD wastes investigated. Wherever possible, these tests results are discussed in terms of the physical characteristics believed to be responsible for the observed behavior.

In addition to FGD waste disposal in its normal state, the option usually exists to collect or not to collect fly ash simultaneously with the sulfur reaction products. Although this option may appear to increase the unit disposal cost of sludge and fly ash, the combination or recombination of these materials may improve their environmental acceptability by improving the physical performance of the waste for a particular end use and, thus may decrease the overall disposal cost because of the change in physical properties. Selected tests were conducted on FGD wastes to which fly ash was recombined to determine both their environmental acceptability and their physical behavior for structural and landfilling applications.

6.2 SOLIDS CHARACTERIZATION

The physical properties of any liquid-solid mixture are dependent upon the characteristics of both the liquid and the solid constituents, as well as the interaction between them. The FGD wastes are such mixtures and contain four principal crystalline phases: hydrated calcium sulfite, calcium sulfate (gypsum), fly ash, and unreacted limestone or lime (usually appearing as limestone by reaction with atmospheric CO_2). These solid phases exist as fine particulates suspended in an aqueous liquor which is usually saturated with ions of these solids. In addition, an unpredictable amount of calcium chloride or sodium chloride is also present as totally dissolved salts (TDS). A complete chemical characterization of each of the FGD waste materials studied is given in Section VII.

The relative amounts of each of the solid crystalline phases are dependent upon system design parameters and include the sulfur content of the coal and the efficiency of scrubbing, the fly ash in the flue gas passing through the scrubber and the efficiency of the system to remove fly ash, the stoichiometric ratio of reactants added relative to sulfur content and the reactant utilization efficiency, and the amount of oxidation of the sulfur products that takes place in the system. The efficiency of scrubbing sulfur and fly ash from the flue gas and the amount of sulfur product oxidation that takes place are primarily functions of system design, but other factors enter into these processes that include combustion behavior in the boiler, the nature of mineral phases in the coal and its total ash content, the natural reactivity of lime or limestone, and the particle size and distribution of the sulfite particles. The number of independent and interdependent variables that affect the composition and characteristics of the resulting waste product are so numerous and varied that it is not likely that any two sulfur waste products are identical. Furthermore, each crystalline phase with its specific characteristics has an influence on the behavior of the sludge. Characterization of the solid portion of each sludge relative to phase identification and particle characteristics is discussed in Section VII and Appendix A. To the extent possible, correlations between the particular characteristics of these phases and behavior of the sludge are made in subsequent subsections.

6.3 WET BULK DENSITIES

The method of sludge dewatering is a critical variable that affects disposal costs in most cases and determines the selection of the disposal methods in some cases. Measurements of the wet bulk densities of several sludges dewatered by various alternative methods have been previously reported (Refs. 1 and 2) and have demonstrated the greater dewatering capability of filtering or centrifugation relative to settling or free drainage. In most sludges, there was very little difference in the wet density of sludges dewatered by settling as compared to free drainage. In almost every sludge, the particle packing density of these two methods was nearly identical as determined by the maximum wet density or by dry bulk density. The slight improvement in wet bulk density of the drained sludge was credited to the lower water retention made possible by the free draining condition.

In a similar manner, it was shown that the difference in density between filtering and centrifugation was usually quite small (Refs. 1 and 2). It was pointed out that, although filtering was usually slightly superior for dewatering than centrifugation when using laboratory equipment, this difference is not always apparent when using industrial equipment. The water retentive capabilities of all sludges was shown to be so great that in only one sludge dewatered by filtration was maximum dewatering observed. Generally, sludges containing coarser particle size distributions dewatered more effectively by all methods relative to sludges with finer particle size distributions.

In the most recent series of experiments, dewatering measurements were made on five samples originating from three scrubbing facilities: (1) a Tennessee Valley Authority (TVA) Shawnee lime sludge from the venturi-spray tower scrubber collected without fly ash; (2) a sludge identical to (1) to which was added fly ash to 40 wt% of the total solids; (3) a double alkali sludge from the Gulf Power Company (GPC) Plant Scholz collected without fly ash; (4) a double alkali sludge identical to (3) but collected with 30 wt% fly ash; and (5) a lime sludge without fly ash from the Louisville Gas and Electric (LG&E) Paddy's Run station scrubber using a carbide lime sludge absorbent.

6.3.1 Experimental Procedure

The wet bulk density was determined on FGD sludge samples after each was dewatered by settling, settling with free drainage, vacuum filtration, and centrifugation. For each dewatering method, the wet bulk density was determined by measuring the weight and volume of the dewatered sample. Subsequently, these samples were dried to constant weight, from which the solids content of the wet sample was determined.

The true density of each solid was measured by a method of air displacement, using a Beckman air pycnometer. The air pycnometer operates on the principle of Boyle's law in which the volume of air displaced by the sample is accurately measured.

6.3.2 Bulk Density Test Results

The wet bulk density of the five FGD sludges was calculated as a function of solids content from the equation

$$\rho_B = \frac{\rho s \, \rho w}{\rho_w f_s + \rho s(1 - f_s)}$$

where ρ_B is the wet bulk density, ρs and ρw are the true density of the solids and water, respectively, and f_s is the weight fraction solids content. In all previously reported measurements, the measured wet bulk density precisely obeyed this relationship. The relationship between wet bulk density and solids content for each sludge and the values of wet bulk density resulting from dewatering by each method are indicated in Figures 8 through 12.

These figures show that the most effective dewatering method was filtration, and the least effective method was settling for all sludges. These results are in agreement with previously reported measurements. However, in this test series, the centrifuged sludge did not dewater as effectively as the sludge previously reported. The most probable reason for this difference in behavior was the fine particle size of sludge particles in this test series, which do not respond as well to centrifugal forces. A summary of wet bulk density as a function of dewatering method for these five samples and eight samples previously tested is presented in Table 14.

A significant result was observed in the freely drained Shawnee lime sludge to which fly ash was added. The solids content was adjusted to approximately 25 percent to simulate clarifier underflow for this sludge. When poured into the test container, the coarser fly ash particles (typically 50 μm in diameter) settled more rapidly than the sulfur-phase particles typically 20 μm in diameter) and formed a fly ash layer on the filter paper used as a retainer. Supernate water then drained through as in all other cases, but the presence of a fly ash layer beneath the sludge appeared to aid dewatering. Because water retention in fly ash is relatively low, all the supernate water passed through this fly ash layer and created air voids. However, since the fly ash is contiguous with the sulfur phase, surface tension forces between the fly ash particles and water are capable of overcoming the surface tension between sulfur phase particles and water. Thus, much of this water is removed from the sludge, and it too is passed through the fly ash layer. The net consequence of this action is that more effective dewatering takes place, which is nearly as effective as filtration. Results from other bench-scale tests and several ponds at the Shawnee Field Evaluation project where underdrainage is employed were a consequence of this phenomena; these data are presented in the report on that study (Ref. 4).

6.4 VISCOSITY

The ability to transport sludge either by pumping through pipelines or by truck is dependent upon the ease (or resistance) of the sludge to flow as a function of retained water. In a previous report (Ref. 1), it was shown that pumpable mixtures (< 20 poise) range from a high solids content of 70 percent to a low solids content of 32 percent. Conversely, sludges having sufficient resistance to flow for truck transport range as low as 45 percent solids to a high of 80 percent solids. An evaluation of the previously reported data indicated that the presence of fly ash contributed strongly to the fluidity of the sludge. Additionally, at equivalent water contents, fine-particle sludge had high viscosity whereas coarse sludge had low viscosity. There also appeared to be a subtle effect related to particle morphology, but this effect could not be separated from the particle size effect in the data.

6.4.1 Experimental Procedure

The viscosity measurements were performed at room temperature using a S & A VT-02 viscometer having a cylindrical sleeve immersed

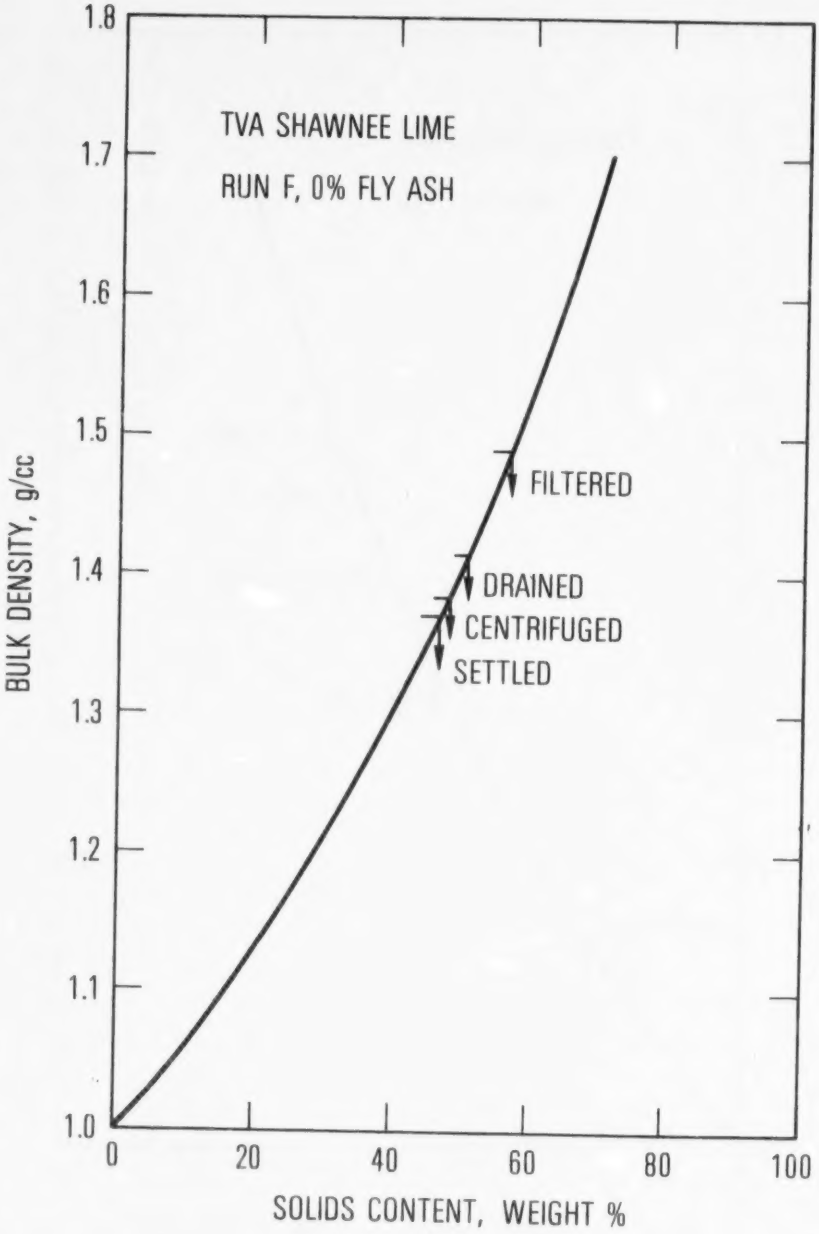

Figure 8. Bulk density as a function of solids content: TVA Shawnee lime sludge without fly ash

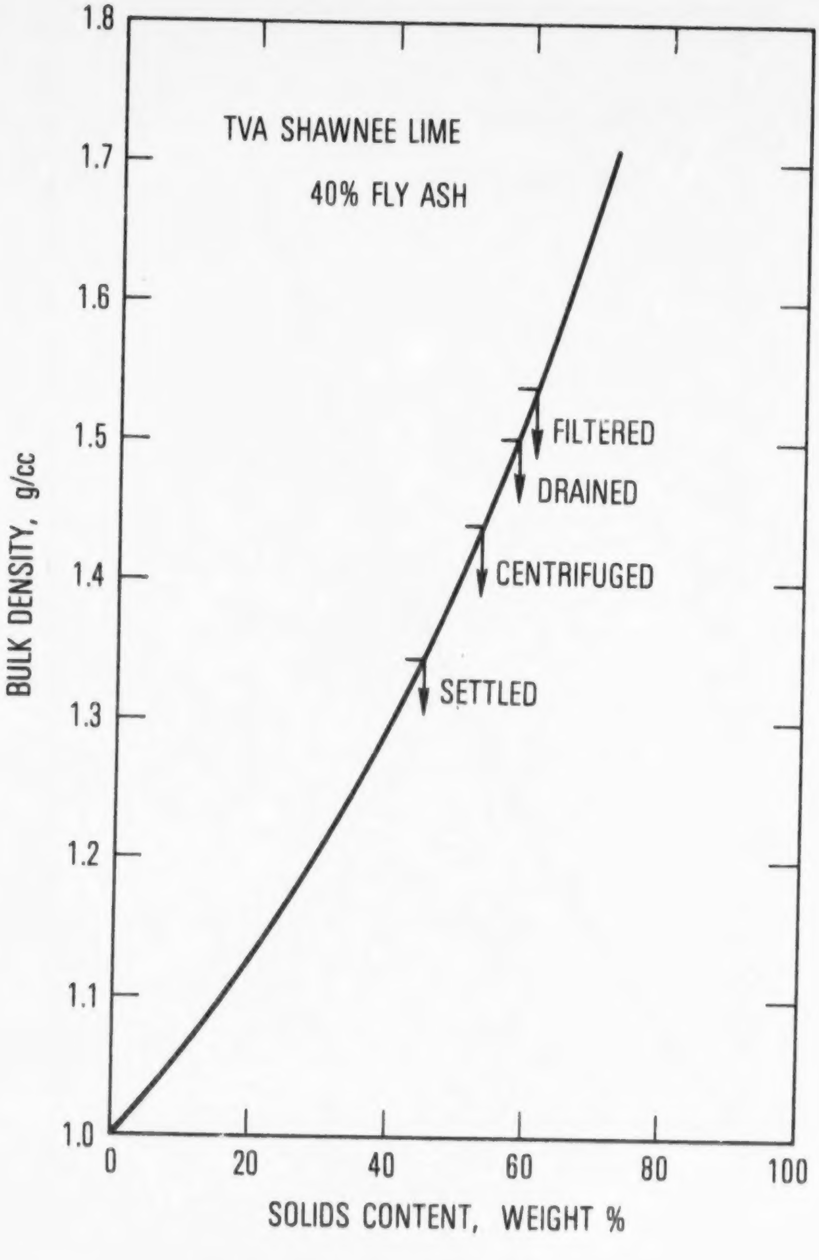

Figure 9. Bulk density as a function of solids content: TVA Shawnee lime sludge with 40-percent fly ash

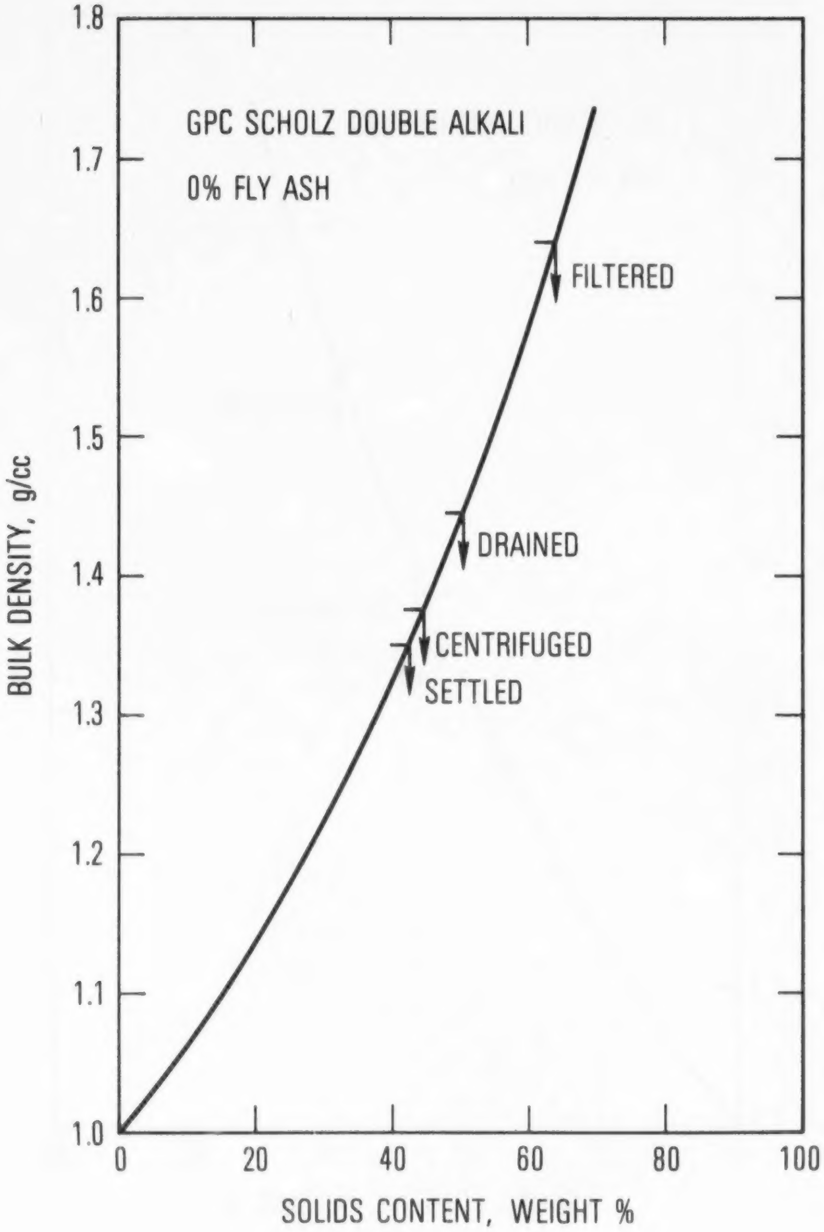

Figure 10. Bulk density as a function of solids content: GPC Plant Scholz double-alkali sludge without fly ash

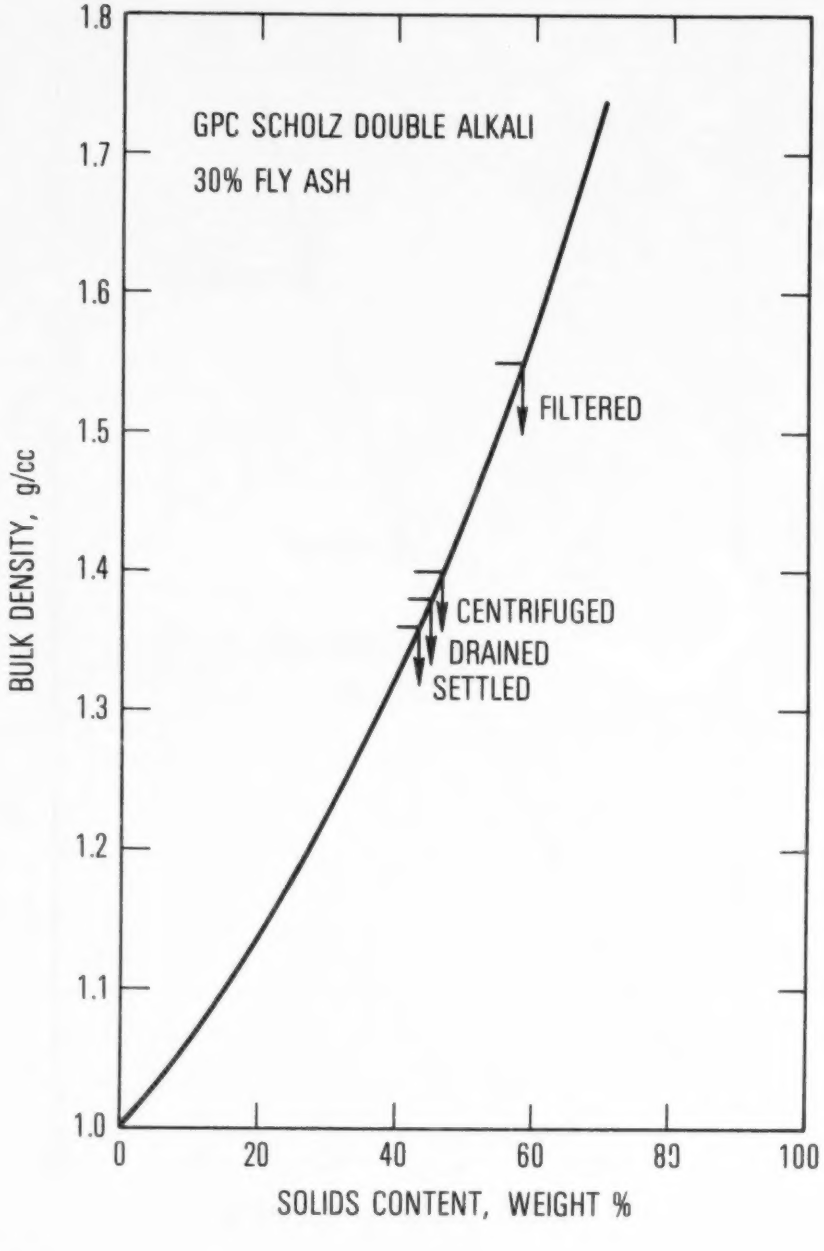

Figure 11. Bulk density as a function of solids content: GPC Plant Scholz double-alkali sludge with 30-percent fly ash

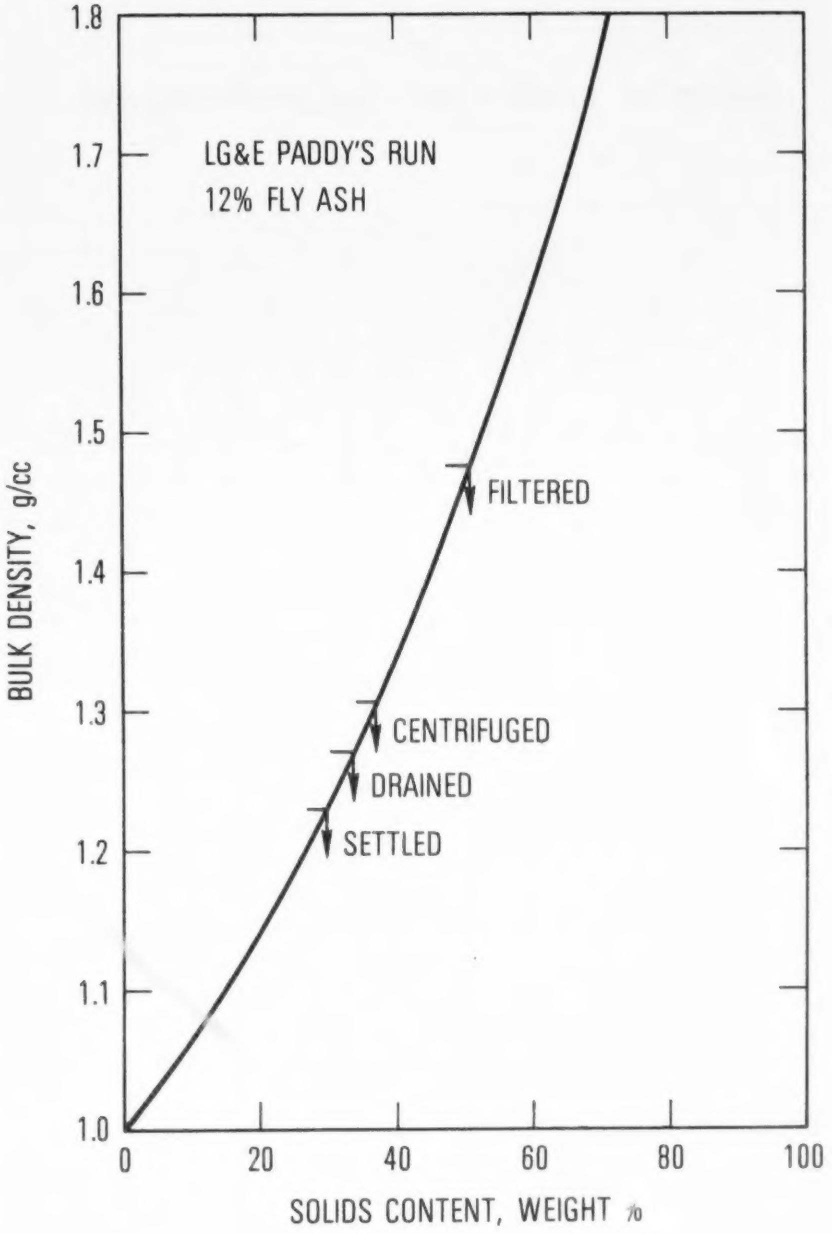

Figure 12. Bulk density as a function of solids content: LG&E Paddy's Run carbide lime sulfur sludge with 12-percent fly ash

TABLE 14. SAMPLE SOURCES AND DENSITIES

Sample Source and Date	Dewatering Method							
	Settled		Settled and Drained		Centrifuge		Filter	
	Percent Solids	Density, g/cc	Percent Solids	Density, g/cc	Percent Solids	Density, g/cc	Percent Solids	Density, g/cc
Shawnee Limestone, 2/1/73	49.0	1.45	55.7	1.51	59.8	1.56	65.0	1.65
Shawnee Limestone, 6/15/74	52.9	1.46	58.3	1.53	63.3	1.60	65.9	1.64
Shawnee Lime, 3/19/74	41.5	1.34	43.4	1.36	49.9	1.44	56.0	1.51
GM Double Alkali, 7/18/74	40.0	1.31	43.9	1.35	50.9	1.43	57.8	1.52
Utah Double Alkali, 8/9/74	37.2	1.30	41.4	1.33	62.2	1.62	54.6	1.50
Duquesne Lime, 6/17/74	47.6	1.40	53.1	1.48	57.2	1.52	57.0	1.52
Cholla Limestone, 9/1/74	46.7	1.39	50.9	1.44	60.9	1.58	53.4	1.48
Mohave Limestone, 3/30/73	66.6	1.65	67.2	1.67	77.0	1.86	80.3	1.78
Shawnee Lime, 0% Fly Ash	–	1.37	–	1.42	–	1.39	–	1.49
Shawnee Lime, 40% Fly Ash	–	1.35	–	1.50	–	1.44	–	1.54
Scholz Double Alkali, 0% Fly Ash	–	1.35	–	1.44	–	1.38	–	1.61
Scholz Double Alkali, 30% Fly Ash	–	1.36	–	1.38	–	1.40	–	1.55
LG&E Carbide Lime, 12.4% Fly Ash	–	1.23	–	1.27	–	1.31	–	1.48

in the FGD fluid waste and rotating at 64 rpm. The 2.4-cm (15/16-in.) diameter rotating sleeve generates a shear rate of 7.9 cm/sec (15.6 ft/min) at its outer surface. The range of viscosities that can be measured with this sleeve is 3 to 150 poise. (Water has a viscosity of 0.01 poise.) At values of viscosity greater than 120 poise (which is beyond the limit of interest), an anomalous decrease in measured viscosity of the sludge was observed, which was interpreted as a separation of liquid and particles at the interface with the rotating sleeve.

Prior to viscosity measurement, the solids content of the sludge was determined, and the mixture was homogenized by hand stirring. The cylindrical sleeve was then immersed in the sludge and left undisturbed for 15 sec, at which time the stirring motion ceased. The viscometer was then turned on, and the viscosity was noted.

Viscosity measurements were made on six samples originating from four scrubbing facilities: (1) a Shawnee lime sludge from the venturi-spray tower scrubber collected without fly ash, (2) the identical sludge to which was added fly ash to 40 percent of the total solids, (3) a Shawnee limestone sludge from the turbulent contact absorber (TCA) scrubber collected without fly ash, (4) a double alkali sludge from the Plant Scholz collected without fly ash, (5) the same double alkali sludge collected with fly ash, and (6) a lime sludge from the LG&E Paddy's Run station scrubber using carbide lime sludge absorbent. The viscosity data from these sludges are presented in Figure 13, superimposed on the data reported previously for ease of comparison.

The Shawnee lime and Shawnee limestone sludges without fly ash have nearly identical viscosity relationship, both being at lower solids content than the sludges with fly ash. When fly ash was added to the Shawnee lime sludge, the resulting viscosity displaced to a higher solids content as expected, but the resulting curve was not coincident with the previously measured Shawnee lime sludge having identical fly ash content. The difference between the two lime sludges with fly ash was a much larger sulfite rosette size of the more recently measured sludge. The displacement was exactly parallel at 3 percent greater solids content in the larger sized sludge.

The Paddy's Run station sludge sample was a fine-grained material, having approximately 12 percent fly ash, and behaved similarly to the previously reported double alkali sludges. This sludge had a rapidly rising viscosity at relatively low solids content; this behavior is believed to be caused by the small particle size of the sludge, similar to the double alkali sludges.

The Plant Scholz sludge was also a double alkali sludge and also fine-grained, but it did not behave like the other double alkali sludges. The viscosity curves for both Scholz sludges (one with and the other without fly ash) have relatively high solids contents similar to the lime/limestone sludges. The sludge with fly ash showed no significant difference from the sludge without fly ash. From an examination of the morphology of the sludge

CURVE	SLUDGE	FLY ASH, %	DATE
1	GM PARMA DOUBLE ALKALI	7.4	7/18/74
2	UPL GADSBY DOUBLE ALKALI	8.6	8/9/74
3	TVA SHAWNEE LIME	40.5	3/19/74
4	DLC PHILLIPS LIME	59.7	6/17/74
5	TVA SHAWNEE LIMESTONE	20.1	2/1/73
6	TVA SHAWNEE LIMESTONE	40.1	6/15/74
7	TVA SHAWNEE LIMESTONE	40.9	7/11/73
8	LG&E PADDY'S RUN CARBIDE LIME	12.4	7/76
9	TVA SHAWNEE LIME	<1.0	9/8/76
10	TVA SHAWNEE LIMESTONE	<1.0	9/28/76
11	GPC SCHOLZ SODA ASH DOUBLE ALKALI	<1.0	6/20/76
12	GPS SCHOLZ SODA ASH DOUBLE ALKALI	30.0	6/27/76
13	TVA SHAWNEE LIME	40.0	9/8/76

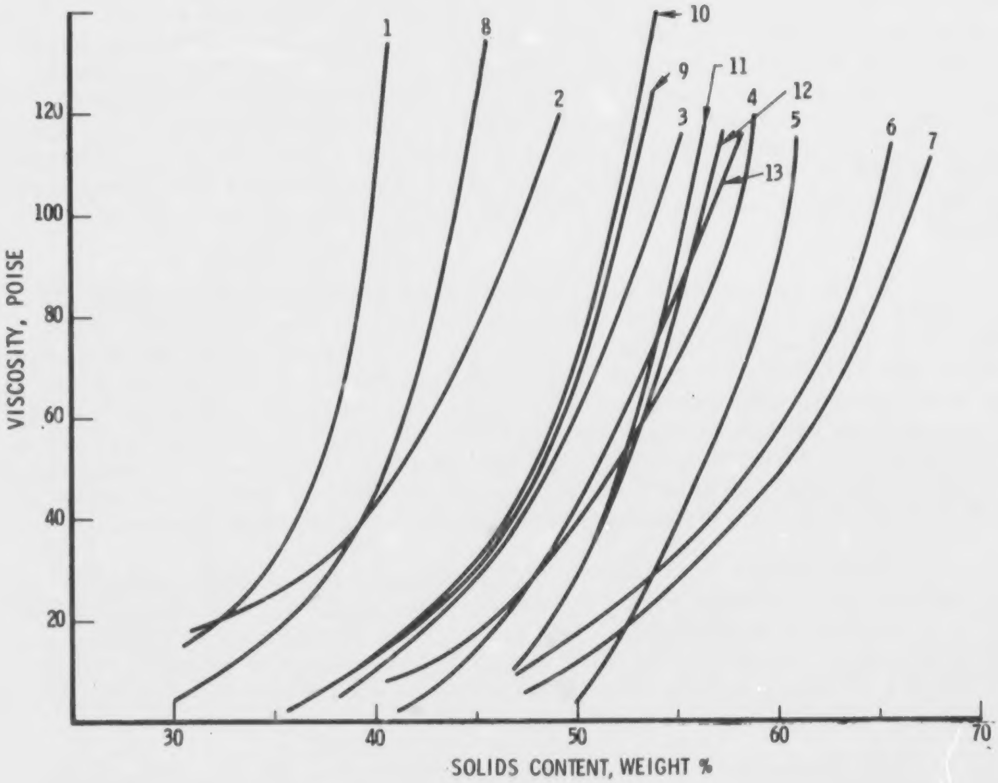

Figure 13. Viscosity of FGD Sludges

(Appendix A), it is seen that the fine-grained sludge is strongly agglomerated such that the resulting rheological properties are dependent upon the coarseness of the agglomerates rather than the fineness of the individual particles. When fly ash is present at the same solids content, there is a substitution of these agglomerates by fly ash. The fly ash has generally fewer particle sizes than the agglomerates and are nonspherical, typical of cyclone boiler ash. Thus, the viscosity curve is not displaced to a higher solids content as might be expected but appears to be displaced slightly to a lower solids content.

6.4.2 Experimental Results

The results from the viscosity data are consistent with those previously obtained, but additional emphasis is placed on the role of particle or agglomerate size in the rheological behavior. In Figure 13, the three sludges that have relatively high viscosities with a low solids content are all fine-grained and contain very little fly ash. The sludges that retain fluidity until a very high solids content is reached are coarse-grained; the sludge with the highest fluidity has coarse platey grain and a very high fly ash content. Fine-grained sludges that agglomerate show a response much like that of coarser sludges. It appears that platey morphology and fly ash both provide fluidity to a sludge, on the basis of a comparison of the sludges from the Shawnee Station.

The conclusion from these data indicates that particle size, particle morphology, and fly ash all make a contribution to the rheological response of a sludge. Although trends have been determined, it is not now possible to accurately predict the viscosity of a sludge. However, with these data, the estimation of a viscosity curve for a sludge for which a single viscosity value has been determined should be satisfactory for estimating initial operating parameters.

6.5 COEFFICIENT OF PERMEABILITY

The percolation of rainwater through FGD sludge and its ultimate recharge to the water table constitutes a major method by which these sludges can pollute the environment. Methods of disposal are available to prevent or minimize the amount of rainwater that can pass through the sludge. However, the degree of control and the complexity and cost thereof may depend appreciably upon the self-control afforded by the sludge material itself. The measurement of the coefficient of permeability provides a value from which the amount of leachate from a disposal basin can be calculated under any given set of environmental or disposal management conditions.

Permeability measurements of sludges previously reported (Refs. 1 and 2) have shown that most sludges as they might appear in a disposal basin (either by settling or as filter cake) have coefficients of permeability in the approximate range of 2×10^{-4} to 5×10^{-5} cm/sec. A relationship was found for the coefficient of permeability as a function of the volume fraction of solids (complement of pore volume). The effect of a higher volume fraction of solids, either by compaction or consolidation of the sludge, was to decrease the coefficient of permeability. The amount of decrease in permeability and the effect of compaction or consolidation appeared to be a function of the particle size of the sludge and the size and distribution of the fly ash particles.

6.5.1 Experimental Procedure

In the previously reported work, several methods were used to prepare a column for permeability measurements. It was found that the method affected the value of the coefficient of permeability only to the extent that each method would affect the packing density of particles (volume fraction solids). Thus, the method that most accurately simulates a sludge settled (or drained) in a pond was the method chosen for these tests. This method uses a slurry of the sludge poured into a column and allowed to settle or drain as it might in a disposal basin. Pore volume is calculated from the volume of settled solids, the known weight of solids, and the true density of the solids. (Filter cake has a pore volume similar to a settled and drained slurry.)

The permeation measurements were begun when all untreated water dripped through the column. Deionized water was then added to a known height above the top of the sludge, and the amount of water percolating through the column was collected and measured as a function of time.

Additional columns with Shawnee lime, LG&E Paddy's Run, and Gulf Scholz sludges were prepared in the same manner, but before deionized water was added, the materials were consolidated under 30 or 100 psi loads. A load of 30 psi is approximately the force experienced at the base of a 40-ft disposal site, and the permeability of the sludge consolidated under that force represents a value that may control the movement of leachate through the waste. At a load of 100 psi, the consolidation of the sludge represents an assumption of lower limit to the permeability. The permeability coefficients were determined by the method previously described.

6.5.2 Experimental Results

The results of the permeability measurements of untreated sludges analyzed during this phase are shown in Table 15. Because considerable data had been generated in previous analyses of untreated sludges (Figure 14), permeability coefficients were determined for these materials after compaction under 30- and 100-psi loading. In Figure 14, it can be seen that most untreated sludges have permeability coefficients in the range of 10^{-3} to 10^{-4} cm/sec, but the compacted materials (Table 15) have coefficients of approximately one order of magnitude lower, i.e., 10^{-4} to 10^{-5}. Specific cases are discussed below.

For the case of the TVA Shawnee lime sludge, the extrapolation of the previous data to higher values of solids fraction is a reasonable representation of the sludge consolidated at high pressures. These data

TABLE 15. PERMEABILITY COEFFICIENTS OF COMPACTED UNTREATED SLUDGE

Sludge Source	Sampling Date	Fractional Solids Volume	Permeability Coefficient cm/sec.	Consolidation Pressure (psi)
TVA Shawnee Lime (6% Fly Ash)	9/08/76	0.35	8.9×10^{-6}	100
		0.33	1.9×10^{-5}	30
TVA Shawnee Lime	9/08/76	0.47	7.3×10^{-6}	100
		0.42	1.1×10^{-5}	30
		0.41	1.4×10^{-5}	30
LG&E Paddy's Run (12% Fly Ash)		0.25	8.4×10^{-6}	100
		0.21	3.4×10^{-5}	30
GPC Scholz (Without Fly Ash)	6/20/76	0.37	1.4×10^{-4}	100
		0.34	4.4×10^{-4}	30
GPC Scholz (30% Fly Ash)	6/27/76	0.36	4.8×10^{-5}	100
		0.34	8.3×10^{-5}	30

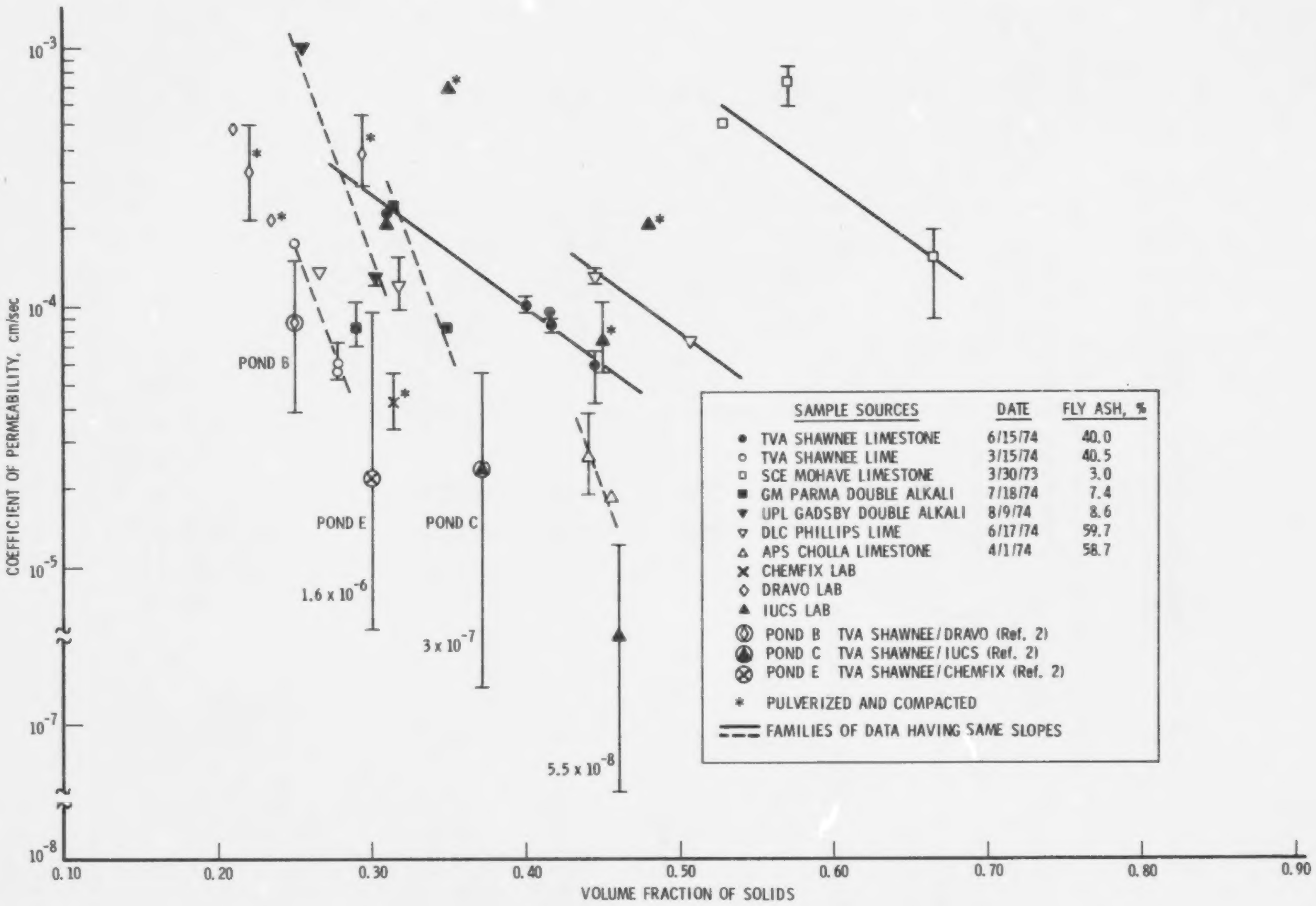

Figure 14. Permeability of chemically treated and untreated sludges

indicate that an expected lower limit of permeability may be in the range of 10^{-5} cm/sec. The data for the Shawnee lime sludge to which 40-wt% fly ash was added show permeabilities similar to the sludge without fly ash but at a higher solids fraction. This is believed to be a consequence of less than complete mixing of the sludge and fly ash.

The permeability coefficients for the compacted GPC Plant Scholz sludges was approximately 10^{-4} cm/sec. The sludge without fly ash had permeabilities about five times higher than the sludge with fly ash, but the solids fraction was nearly identical for both materials. The explanation is believed to be related to the agglomeration of the fine sludge particles, which respond much like coarser materials; without fly ash, passage of water through it is relatively rapid. When fly ash was present the solids fraction did not change, as the fly ash, having a broad particle size distribution, fills pore passages such that water passage rate through the waste is reduced. The bimodal particle distribution between coarse sludge and fine fly ash in the Arizona Public Service (APS) Cholla sludge was previously shown (Ref. 1) to produce the same effect.

The LG&E sludge was a fine particle sulfite sludge that did not consolidate well and did not reach a high solids fraction even under high loads. Moreover, surface tension forces between fine particles and water is high, and these forces must be overcome for water to pass through. Thus, the low permeability shown for this sludge is believed to be a consequence of the particle size of the sulfite phase.

The results from the measurement of permeability coefficients indicate that sludges that are disposed of by either settling or by placement of filter cake will have permeabilities generally between 5×10^{-5} to 2×10^{-4}. Generally, coarser particles settle to higher fraction solids and have higher permeability coefficients (such as the Mohave sludge) than fine particle sludges. When the presence of fly ash gives the waste a bimodal particle distribution, such as the sludges from Cholla, the permeability tends to be less than otherwise expected. Fine particle sludges do not settle or consolidate well, but because of high surface tension forces, their permeabilities tend to be lower than those of coarse particle sludge with an equivalent solids fraction content. Consideration of sludge equivalent to that occurring at the base of a 40-ft high disposal site will decrease permeabilities to about 10^{-5} cm/sec.

6.6 BEARING STRENGTH

Preliminary measurements of the load-bearing strengths of two FGD sludges were reported in Reference 1. Since that time, alternative dewatering methods have been employed, and the method of testing has been slightly modified. Recent measurements of load-bearing strengths as functions of solids content have been made for a number of sludges. These results complement the previous data and serve to reinforce the conclusions drawn from them, namely, that sludges may be dewatered to critical values of solids content above which the load-bearing strengths increase steeply to values well above the minimum for safe access of personnel and equipment.

6.6.1 Test Procedure

Load-bearing strengths were measured for sludges from six power plants, using a method substantively similar to the standard bearing ratio test for soils (Ref. 11). A 0.95-cm-diameter (3/8-in.) rod was forced into the sludge at a constant rate of 0.25 cm/min (0.1 in./min) with an Instron loading machine. Penetration loads were recorded continuously to a maximum penetration depth of 2.54 cm (1 in.). The cylindrical sample container was sufficiently large, 7-cm (2.7-in.) diameter by 10-cm (4-in.) depth, that edge and bottom effects were negligible. Tests were also made with 1.27-cm (0.5-in.) and 2.54-cm (1-in.) diameter rods which produced the same load-penetration curves for all three rods and confirmed that rod size was not a variable in these measurements. Samples of partially dewatered sludge, which initially had negligible load strength, were placed in the containers on a 1.27-cm (0.5-in.) deep layer of sand. The containers had perforated bottoms to allow the sludge to dewater by means of underdrainage. Load-penetration curves were obtained for each of four solids contents as the samples dewatered. Solids contents were obtained by vacuum oven drying of small specimens removed from the top of the sample immediately after each test.

6.6.2 Test Results

The loads measured at the maximum penetration depth of 2.54 cm (1 in.) were plotted against the corresponding solids contents in Figure 15 for 11 sludge compositions. The lime process sludge from the TVA Shawnee Station was tested as received, as well as after intermixing 40-wt% fly ash (dry basis). The curves of Figure 15 show that similar strengths can be expected from both samples, but at a proportionally higher solids content for the sample containing fly ash. The ratio of solids contents of the two samples required to produce a given load is approximately the ratio of bulk densities of underdrained samples. Load strengths at 1-in. penetration in excess of 7 kg/cm^2 (100 lb/in.^{2}) were obtained for ash-free samples with solids content greater than 58 percent and for sludge containing 40-wt% fly ash if the solids content was greater than 65 percent. Negligible strengths were observed for ash-free samples with solids content of less than 51 percent and for samples with 40-wt% ash if the solids content was less than 59 percent.

Double alkali process sludge from the Gulf Scholz plant was essentially ash-free for one sample, while the other sample contained about 31 percent ash. The results of bearing tests of these two samples were qualitatively similar to the results for the TVA Shawnee lime samples, although the separation of the two curves is not as great (Figure 15). However, the data points for the ash-free samples were scattered so that quantitative comparisons are less reliable. It appears that load-bearing strengths in excess of 7 kg/cm^2 (100 lb/in.^{2}) can be expected of ash-free sludge with solids

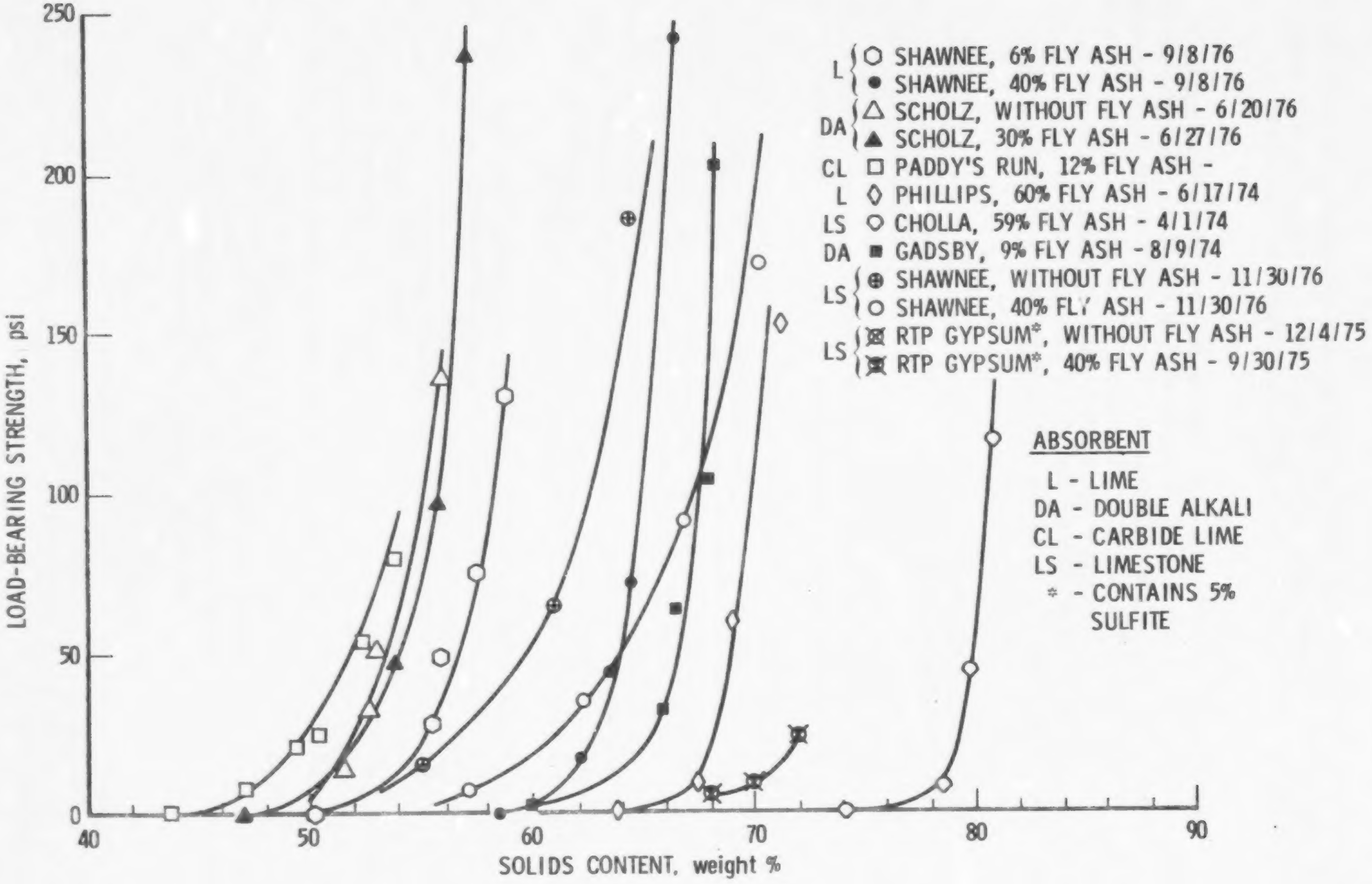

Figure 15. Load-bearing strength as a function of moisture, fly ash, and sludge origin

content greater than about 55 percent and for sludge containing 30 percent ash if the solids content is greater than about 56 percent. Negligible strengths were observed for both samples if the solids contents were less than 48 percent.

Results of compaction strength tests on a sample of carbide process sludge produced at the LG&E Paddy's Run station are also shown in Figure 15. Dewatering of this sample was not continued beyond 52.5 percent solids, which corresponds to a load-bearing strength at one-inch penetration of 4 kg/cm^2 (57 lb/in.^{2}). The curve for LG&E sludge appears to have the same shape as the curve for the Scholz ash-free sludge (Figure 14). Negligible strength was observed for samples with solids contents of less than 44 percent.

Sludge from the double alkali process was obtained from the Utah Power and Light (UPL) Gadsby station. This sludge was tested for load-bearing strength as it dewatered by means of underdrainage. Results of the tests plotted in Figure 14 show that a load-bearing strength in excess of 7 kg/cm^2 (100 lb/in.^{2}) was developed when the solids content became greater than 68 percent. Below 60 percent solids, negligible strength was observed.

The compaction strength versus solids content curve for lime process sludge containing fly ash from the Duquesne Light Company (DLC) Phillips station was similar in shape to other sludges previously described, although it was displaced toward a higher solids content, as shown in Figure 14. Load-bearing strengths in excess of 7 kg/cm^2 (100 lb/in.^{2}) were observed for solids contents greater than 70 percent, and negligible strengths were found at solids contents below 65 percent. Although not plotted in Figure 14, a load-bearing strength of 33 kg/cm^2 (470 lb/in.^{2}) was measured when the sample had dewatered to a solids content of 73 percent.

Limestone sludge from APS Cholla was tested for load-bearing strength. This sludge had to be dewatered to the highest solids content of all sludges tested before it developed significant strength. At a solids content of less than 76 percent, the sludge showed negligible strength. Load-bearing strengths in excess of 7 kg/cm^2 (100 lb/in.^{2}) were observed with solids contents greater than approximately 80 percent. Although not shown in Figure 15, a load-bearing strength greater than 44 kg/cm^2 (630 lb/in.^{2}) was observed for the Cholla sludge sample when the solids content reached 83 percent.

Limestone process sludge (35 wt% solids)[*], containing less than 3 percent fly ash, was taken directly from the clarifier underflow at TVA Shawnee and was tested as received. Also tested was a sample to which was admixed 40-wt% (dry basis) fly ash, without any preliminary dewatering.

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[*] This sludge slurry had a high settling rate. Under examination with the SEM, some very large crystals of $CaSO_3 \cdot 1/2\ H_2O$ (>2 µm in length and >0.2 µm in thickness) were observed.

The compaction strength versus solids content curves for the Shawnee limestone and limestone with fly ash samples (Figure 15) are slightly different in shape from those typical of the other sludges tested. A greater spread was observed between the solids contents corresponding to a just measurable load-bearing strength (52 percent for the sludge and 55 percent for the sludge with fly ash mixture) and the solids contents corresponding to a load-bearing strength greater than 7 kg/cm^2 (100 lb/in.^{2}), 63 and 67 percent, respectively. Although this might have been caused by the low initial solids content of the clarifier underflow, a similarly shaped curve was reported previously (Ref. 1) for the compaction strength of Shawnee limestone sludge. As expected, the addition of fly ash displaced the compaction strength curve toward a higher solids content, without significant alteration of the shape.

It is apparent that each of these 11 sludges can be dewatered by a simple drainage process to a solids content which corresponds to a load-bearing strength well in excess of the minimum required for accommodating powered equipment, and, in most cases, a load-bearing strength suitable for construction can be obtained.

SECTION VII

CHEMICAL CHARACTERIZATION OF SLUDGE LIQUORS AND LEACHATES

7.1 BACKGROUND

Previous laboratory characterization and chemical analyses were performed on sludge from six flue gas desulfurization (FGD) waste sources, and the results of these experiments have been reported (Ref. 1). The chemical characterization of sludge from three additional sources is herein reported. The primary objective of this task was to investigate the effect of the presence of fly ash in the flue gas being scrubbed on the concentrations of trace elements in the sludge liquors and leachates. All of the sludges previously analyzed contained fly ash which varied from 20 to 60 percent, except for three which contained 3 to 9 percent. Previously reported analyses for trace elements in system liquors and leachates were only for those sludges produced in FGD scrubbing systems that collected some or all of the fly ash in the scrubber. Therefore, it was not possible to determine unequivocally whether the trace elements in the liquors and leachates resulted from the scrubbing of fly ash. It was necessary, therefore, to analyze sludges from scrubbing operations in which fly ash was removed from the flue gas ahead of the scrubber.

Additionally, leaching tests were performed with sludge and fly ash mixtures, prepared by the addition of fly ash to ash-free FGD sludge, and also with fly ash alone using leaching water controlled at a pH ranging from 4 to 9. A comparison was made of the concentrations of trace elements in the liquors and leachates from ash-free sludge and sludge containing fly ash for two power plants for the purpose of identifying the source of these species. An attempt was made to correlate the magnitude of the measured trace element concentrations in sludge liquors and leachates with fly ash, pH, and conditions of scrubbing or leaching.

A secondary objective of this task was to provide a broader base for the chemical characterization of FGD sludges. The previous study (Ref. 1) showed that the waste liquors were saturated with gypsum in their disposal state. The liquors from the sludges herein reported were analyzed for major and minor constituents and compared with the existing data base to determine their relative state of chemical saturation.

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7.2 DESCRIPTION OF POWER PLANT SCRUBBING FACILITIES, SAMPLING, AND CHEMICAL ANALYSES

The chemical characterization for this study was generated from samples taken from the three power plant scrubbing systems listed in Table 16, using lime or double alkali systems and Eastern coals. For the purpose of this study, the effect of fly ash collection alternatives was investigated relative to the scrubber waste chemistry and the potential of these wastes as an environmental pollutant source. The sludge from the Tennessee Valley Authority (TVA) Shawnee system was evaluated in the ash-free state in which it was collected, as well as in a recombined state representing the phase constituents as they would have been if no fly ash was collected upstream of the scrubber. The sludge from the Gulf Power Company (GPC) Plant Scholz was evaluated in the ash-free and combined ash and sludge states as they were collected.

Essentially ash-free lime process filter cake was obtained from TVA Shawnee. This sludge was analyzed as received, as well as after mixing with 40 wt% fly ash (dry basis). The fly ash was 67 percent mechanically separated and 33 percent electrostatically separated ash. Two samples of sludge from the double alkali process at the Gulf Scholz station were supplied by A. D. Little, Inc. One sample contained approximately 31 percent fly ash, and the other had no fly ash. A fifth sludge sample tested was obtained from the carbide lime process at Louisville Gas and Electric (LG&E) Paddy's Run station and supplied by Combustion Engineering, Inc. The sludge from this power plant contained approximately 12 percent fly ash. No sludge from this power plant had previously been tested; therefore, the test data were obtained to enlarge the data base for FGD sludge characterization even though no data were available for ash-free sludge to determine the influence of fly ash.

7.3 CHEMICAL ANALYSES

7.3.1 Experimental Procedure

As a general procedure, samples were taken by the scrubber system operating personnel. Some samples were filtered at the site to stop reactions between liquor and solid reagents. All samples were packaged in plastic containers and shipped to The Aerospace Corporation.

Upon receipt of these samples at the laboratory, all slurry samples were filtered through Whatman No. 40 filter paper, and the pH of the filtrate was determined at once. Liquid samples were stored in sealed polyethylene bottles. Solids samples were stored in sealed polyethylene storage bags. Samples were stored for a few days, and in some cases for several months before being analyzed. The time factor had no effect on sludge chemistry except for insignificant reductions of pH and total alkalinity due to absorption of CO_2.

All chemical analyses were performed by standard chemical analysis techniques to at least minimum criteria identified by the U.S. Environmental Protection Agency (EPA) Analytical Quality Control Laboratory

TABLE 16. FGD SYSTEMS SAMPLED AS DATA BASE[a]

Power Plant	Scrubber Type	Scrubbing Capacity MW (equiv)	Coal Source	Absorbent
Tennessee Valley Authority (TVA), Shawnee Steam Plant	Venturi and spray tower, prototype	10	Eastern	Lime
Louisville Gas and Electric Co., Paddy's Run Station, Unit No. 6	Marble bed absorber	70	Eastern	Carbide lime (slaked lime waste)
Gulf Power Company Scholz Plant	Venturi and spray tower	20	Eastern	Soda ash (lime regenerant)

[a] Other pertinent data are given in Tables 1 and 2.

(Refs. 12 and 13). A description of the chemical analyses is presented in detail in Appendix C of Reference 1 for liquids and solids. In every case, both the accuracy and precision of the method were determined with respect to analyses of the scrubber liquors.

Chemical analyses were made for nine trace elements of concern in FGD sludge liquors: arsenic (As), beryllium (Be), cadmium (Cd), copper (Cu), chromium (Cr), mercury (Hg), lead (Pb), selenium (Se), and zinc (Zn). In addition, analyses were made for boron (B), and fluorine (F), which were present at concentration levels much higher than those of the nine trace elements, and for the major constituents calcium (Ca), chloride (Cl), sulfate (SO_4), magnesium (Mg), potassium (K), and sodium (Na). Measurements were made of pH, and total dissolved solids (TDS), and mass balances, charge balances, and gypsum solubility ratios were calculated for each sample to check the internal consistency of the data.

The solid phases of each sludge were identified by examination with the scanning electron microscope (SEM). Analyses were made for each major component of the sludge solids. Comparative analytical data were supplied by A. D. Little, Inc., for the sludge samples from Gulf Scholz.

7.3.2 Results of Chemical Analyses

The results of all chemical analyses performed during this reporting period are presented in tabular form in Tables 17 through 19. The results of the chemical analyses from sources including those previously reported and those herein presented are summarized in Tables 20 and 2. In Tables 17 through 19, the ranges of chemical constituents were obtained from the analyses of the sludge samples taken after the final stage of dewatering.

From these data, several observations can be made that identify the chemical constituent concentrations that may be expected generally from FGD scrubbers. Among the trace elements in sludge liquors, the ranges of concentrations tend to lie between 0.01 and 1 mg/ℓ with the exception of mercury, which has a concentration distribution about 1/10 that of other trace elements. In most sludge liquors, the pH ranges between 6.5 and 9; however, in some samples, pH in the 10 to 12 range was detected. COD ranged between 40 and 140 mg/ℓ .

A correlation exists between the liquor and solids concentrations of beryllium, cadmium, and mercury, in which the values are generally lower than the other elements, in both phases. This appears to indicate that these elements exist in the sludges in relatively minor amounts. On the other hand, solid concentrations are high for Cr and Zn (possibly, also Cu), but corresponding higher concentrations are not observed in the liquor. Whereas, in the first case, the correlation strongly suggests a concentration limitation based on input amounts, in the second case, the lack of correlation suggests that chemical parameters may be controlling the liquor concentrations of these elements.

TABLE 17. CHEMICAL ANALYSIS: SHAWNEE LIME SLUDGE LIQUOR AND LEACHATE[a]

Constituent	Without Fly Ash			Run F + 40% Fly Ash Leachate	
	9/8/76 Run F	9/8/76 Run F Leachate			
	Filtered Sludge Liquor	First Pore Volume	Fifth Pore Volume	First Pore Volume	Seventh Pore Volume
pH	8.0	8.3	7.1	7.9	7.4
TDS	10260	4480	1770	4330	2430
Arsenic	0.058	----	0.120	----	0.360
Beryllium	<0.001	----	<0.001	----	<0.001
Boron	76	35	3	65	16
Cadmium	0.013	----	0.013	---	0.010
Calcium	650	690	450	600	640
Chromium	0.011	0.025	0.010	0.010	0.004
Copper	0.005	0.011	<0.002	<0.002	<0.002
Lead	0.010	<0.002	<0.002	<0.005	<0.005
Magnesium	1730	400	30	310	10
Mercury	<0.00006	----	0.00006	----	0.00024
Potassium	24	14	2	7	4
Selenium	0.078	----	<0.0004	----	0.051
Sodium	137	75	47	72	42
Zinc	<0.001	0.007	0.01	0.003	0.02
Chloride	1320	550	128	400	130
Fluoride	1.9	2.6	2.5	6	1.2
Sulfate	4500	2150	1100	2700	1450

[a] Concentrations in mg/ℓ, as appropriate.

TABLE 18. CHEMICAL ANALYSIS: GPC PLANT SCHOLZ DOUBLE-ALKALI LIQUOR AND LEACHATE[a]

Constituent	6/20/76 Run with No Fly Ash			6/27/76 Run with 30% Fly Ash		
		Leachate			Leachate	
	Filtrate[b]	First Pore Volume	Sixth Pore Volume	Filtrate[b]	First Pore Volume	Ninth Pore Volume
pH	12.1	12.5	12.3	12.0	10.4	9.1
TDS	155700	9140	3550	162700	17330	2140
Arsenic	---	---	<0.004	---	---	0.019
Beryllium	---	---	<0.001	---	---	<0.001
Boron	43	5	<0.5	40	<0.5	<0.5
Cadmium	---	---	0.016	---	---	0.010
Calcium	12	1000	1100	7	550	800
Chromium	---	---	0.0025	---	---	0.024
Copper	---	---	<0.002	---	---	<0.002
Lead	---	---	0.005	---	---	<0.002
Magnesium	0.1	<0.01	<0.01	0.1	0.2	0.3
Mercury	---	---	0.00030	---	---	0.00024
Potassium	320	43	1	380	74	11
Selenium	---	---	<0.0004	---	---	<0.0004
Sodium	53600	2260	12	55300	4720	82
Zinc	---	---	0.007	---	---	0.013
Chloride	5000	1070	310	4900	1050	134
Fluoride	24	48	13	4	3	0.9
Sulfate	80000	3700	1160	84000	10100	1415

[a] Concentrations in mg/ℓ, as appropriate.

[b] Incomplete analysis for filtrate samples is a consequence of insufficient sample quantity.

[c] Approximately 90 percent of the reduction of concentrations occurs by the third PVD.

TABLE 19. CHEMICAL ANALYSIS: PADDY'S RUN SLUDGE LIQUOR AND LEACHATE[a]

Constituent	Filtrate	Leachate	
		First Pore Volume	Tenth Pore Volume
pH	8.9	7.4	8.1
TDS	24230	5240	1650
Arsenic	0.011	---	0.023
Beryllium	<0.001	---	<0.001
Boron	18	2	<0.5
Cadmium	0.025	---	0.004
Calcium	515	410	260
Chromium	0.054	<0.0008	<0.0008
Copper	0.0045	0.004	<0.002
Lead	<0.005	<0.002	<0.002
Magnesium	3400	470	70
Mercury	0.00006	---	0.00006
Potassium	760	125	21
Selenium	0.0028	---	0.006
Sodium	260	40	3
Zinc	0.003	0.015	0.005
Chloride	5600	410	157
Fluoride	<1	<0.1	<0.1
Sulfate	15000	2800	920

[a] Concentrations in mg/ℓ, as appropriate.
12% ash.

TABLE 20. RANGE OF CONCENTRATIONS OF CHEMICAL CONSTITUENTS IN FGD SLUDGE LIQUORS THROUGHOUT THE SCRUBBER LOOP - ALL SOURCES[a]

Scrubber Constituents	Sludge Liquors, mg/ℓ
Aluminum	0.03 to 2.0
Arsenic	0.004 to 0.14
Beryllium	0.001 to 0.18
Cadmium	0.004 to 0.11
Calcium	10 to 2600
Chromium	0.011 to 0.25
Copper	0.002 to 0.56
Lead	0.005 to 0.33
Magnesium	0.1 to 2750
Mercury	0.00005 to 0.005
Potassium	5.9 to 760
Selenium	0.0006 to 0.20
Sodium	10.0 to 55,000
Zinc	0.001 to 0.59
Chloride	420 to 33,000
Fluoride	0.6 to 10
Sulfate	600 to 84,000
Sulfite	0.9 to 3500
TDS	2800 to 162,700
pH	4.3 to 12.7
COD	40 to 140

[a] All test conditions not necessarily standard. See Table 2 for representative list.

An apparent exception is Se, which has the broadest concentration range in the liquor (nearly four orders of magnitude) but has the narrowest concentration range in the solid (factor of eight). In this case, the sample that contributed the high value in the solid had the lowest pH of all samples analyzed.

Among the major chemical species, concentrations and range of concentrations are almost completely dependent upon the chemical parameters of the system. Na, as an example, ranges from a low value of 10 mg/ℓ to nearly 5 percent in the liquid phase in the double alkali system. When high values of Na and sulfate (or Cl) are present, significant amounts of sodium salts may be expected in the solids. The major FGD waste, sulfur phases, can exist as either sulfate or sulfite. As may be expected, the solids sample having the highest sulfite content also had the lowest sulfate content.

One of the most important chemical parameters for the asssessment of the environmental quality of the liquid portion of FGD sludge is the TDS content. In most cases, TDS concentration is typically 10,000 mg/ℓ. Higher values were observed for the double alkali samples and one sample in which a salt brine was used as makeup water. Lower values were observed in two systems during startup and in a third system in a partial open-loop operation. From these data, it is reasonable to expect values of TDS in scrubber liquors to range near 10,000 mg/ℓ for steady-state closed systems, except in cases having exceptional circumstances; these cases can usually be identified from system design parameters.

7.4 LEACHING ANALYSIS

7.4.1 Experimental Procedures

In the previously reported work (Ref. 1), several methods were used to prepare columns, and it was determined that the results were independent of the method. For the work herein reported, the following method was used to prepare a leaching column. Approximately one liter of sludge, as a slurry of about 50 percent solids, was poured into a 6-cm-diameter column containing a porous base plate covered with a filter paper, and the solids were allowed to settle. Excess liquor, including supernate above the settled solids, was allowed to pass through the solids and filter until dripping stopped. Deionized water was added to the column, and the leaching experiment was begun by collecting aliquots of leachate based on pore volume displacements (PVD). Pore volumes were determined from the volume and the solids content of the bed. All column tests were conducted under aerobic conditions.

7.4.2 Results of Leaching Experiments

In previously reported studies (Refs. 1 and 2), leaching tests were continued until 50 pore volumes had been displaced. In most cases, however, it was observed that 90 percent of the decrease in concentration of major leachable species had taken place after 3 pore volumes had been displaced. For the present studies, it appeared unnecessary to continue leaching after 10 pore volumes had been displaced. The complete leaching curves were determined by measurement of the TDS in each sample of leachate. Complete analyses for major and minor constituents were made only on the first and last leachate sample. In Figures 16 through 18, the concentrations of major species (SO_4, Cl, Ca, and Mg or Na) and TDS have been plotted against the average PVD of the leachate for sludges obtained from three power plants. The curves of Figure 16 show the results of leaching Shawnee ash-free lime sludge and also sludge mixed with 40-wt% fly ash. For additional comparison, the concentrations of major species and TDS of the sludge liquor (filtrate taken from vacuum filter) have also been plotted. The TDS in the leachates of both sludge samples decreased from initial values comparable to that of the filtrate and leveled off at 2000 to 2500 mg/ℓ after three pore volumes had been displaced. Similarly, the sulfate leveled off at about 1000 to 1500 mg/ℓ. The calcium concentrations decreased to below the 100 mg/ℓ level. These filtrate and leachate analytical data are also shown in Table 17.

Leachate data were plotted for two sludge samples obtained from Gulf Scholz in the curves of Figure 17; one was essentially ash-free, and the other contained 31 percent fly ash. The corresponding analytical data for the two liquor (filtrate) samples were not plotted because their concentration exceeded the scale of the figure; however, complete data are shown in Table 18. For these sludge samples, the extraordinarily high concentration of dissolved sodium sulfate in the occluded liquor ($>$ 15 percent) was rapidly reduced so that after five pore volumes had been displaced the TDS in the leachate stabilized at about 2200 mg/ℓ. The sulfate concentrations decreased from the 80,000 mg/ℓ level in the liquor and leveled off at 1000 to 1500 mg/ℓ. The calcium concentration increased from about 10 mg/ℓ in the liquor and leveled off below 1000 mg/ℓ. The sodium and chloride concentrations, initially 50,000 and 5000 mg/ℓ, respectively, in the liquor, decreased to levels below 100 mg/ℓ.

The data of Table 19 and Figure 18 show analogous leachate and liquor analytical data for a sludge sample containing fly ash from LG&E Paddy's Run. The leachate from this sludge at the 10th pore volume differed in the last leachate samples from all the other sludges in that the TDS and SO_4 concentrations did not level off at their characteristic values of 2200 and 1300 mg/ℓ. These characteristic values are the result of saturation of the leaching water with gypsum. Lower values observed for the 10th PVD leachate sample from the Paddy's Run sludge represent undersaturation of the leaching water and indicate that most of the gypsum had been already dissolved.

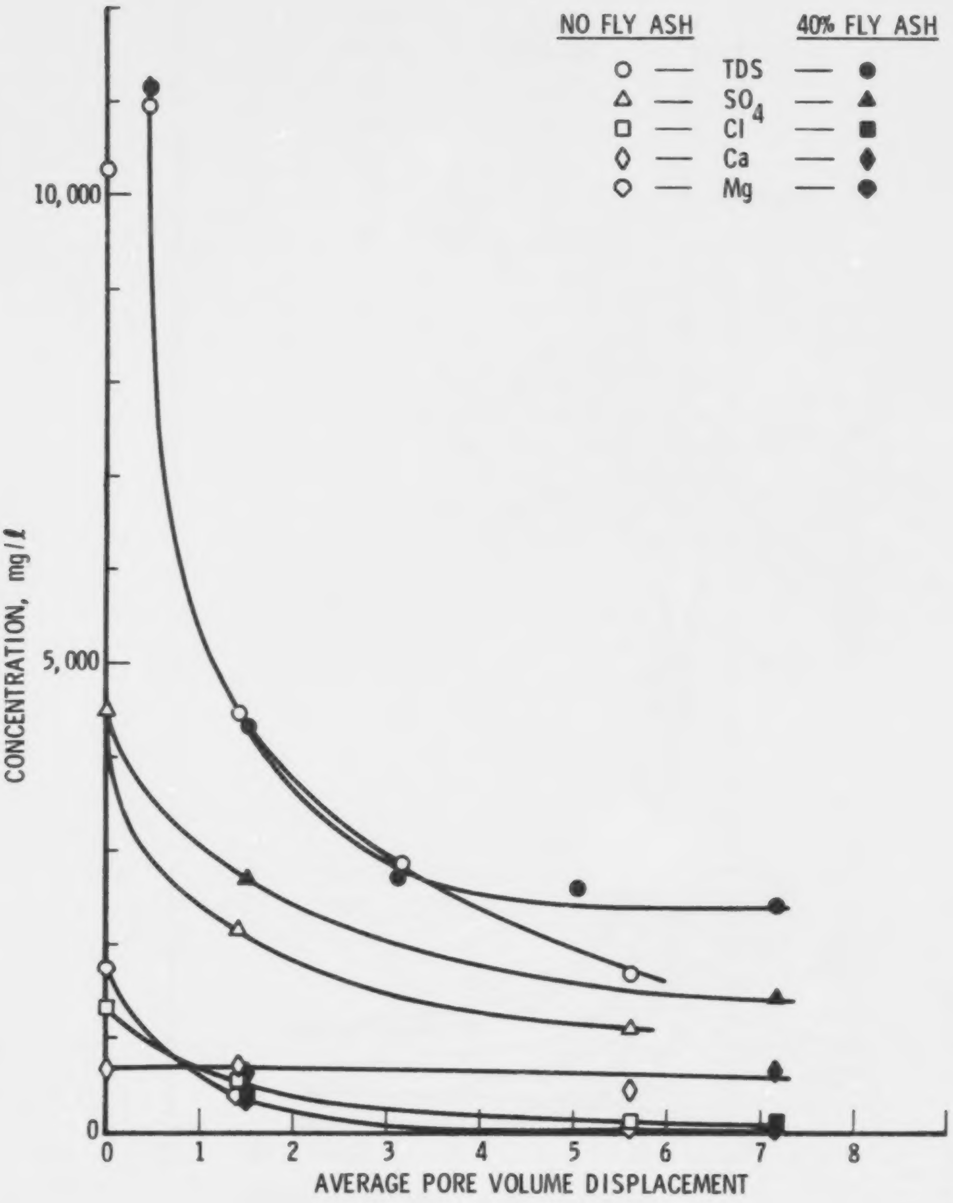

Figure 16. Concentration of major species and TDS in leachate lime sludge with and without fly ash: TVA Shawnee, Run F

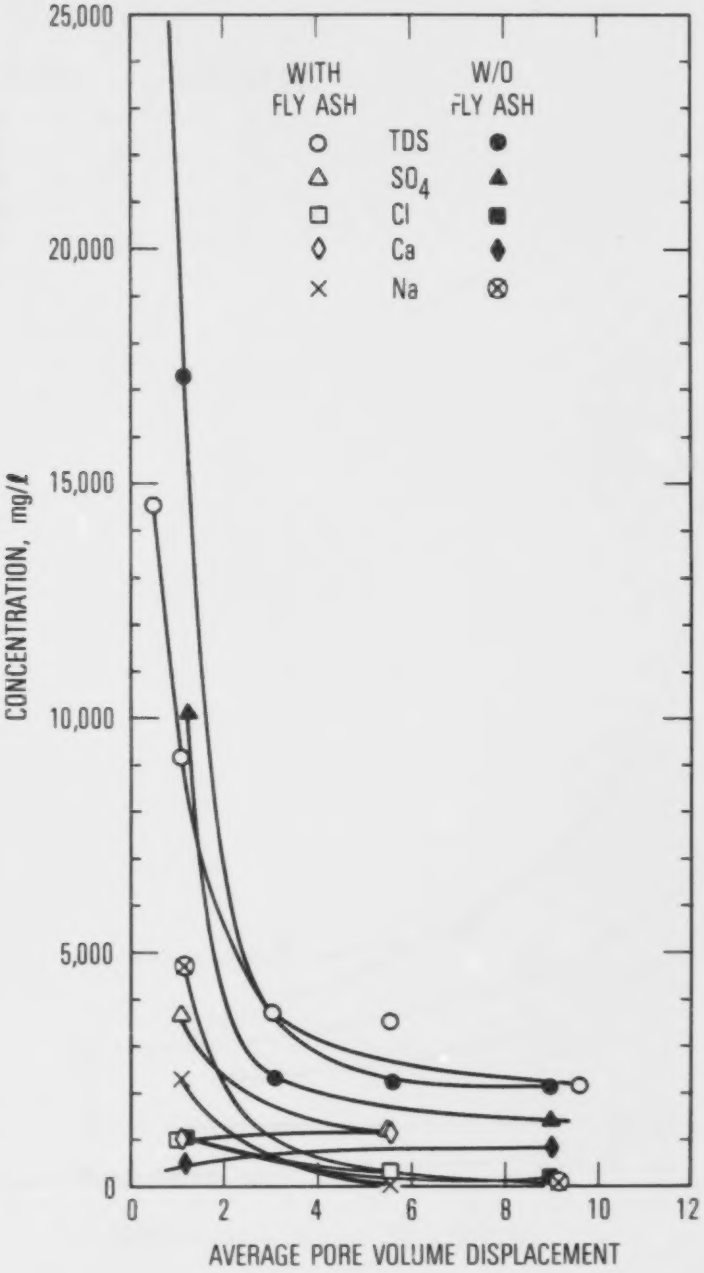

Figure 17. Concentration of major species and TDS in leachate of sludge with and without fly ash:GPC Plant Scholz

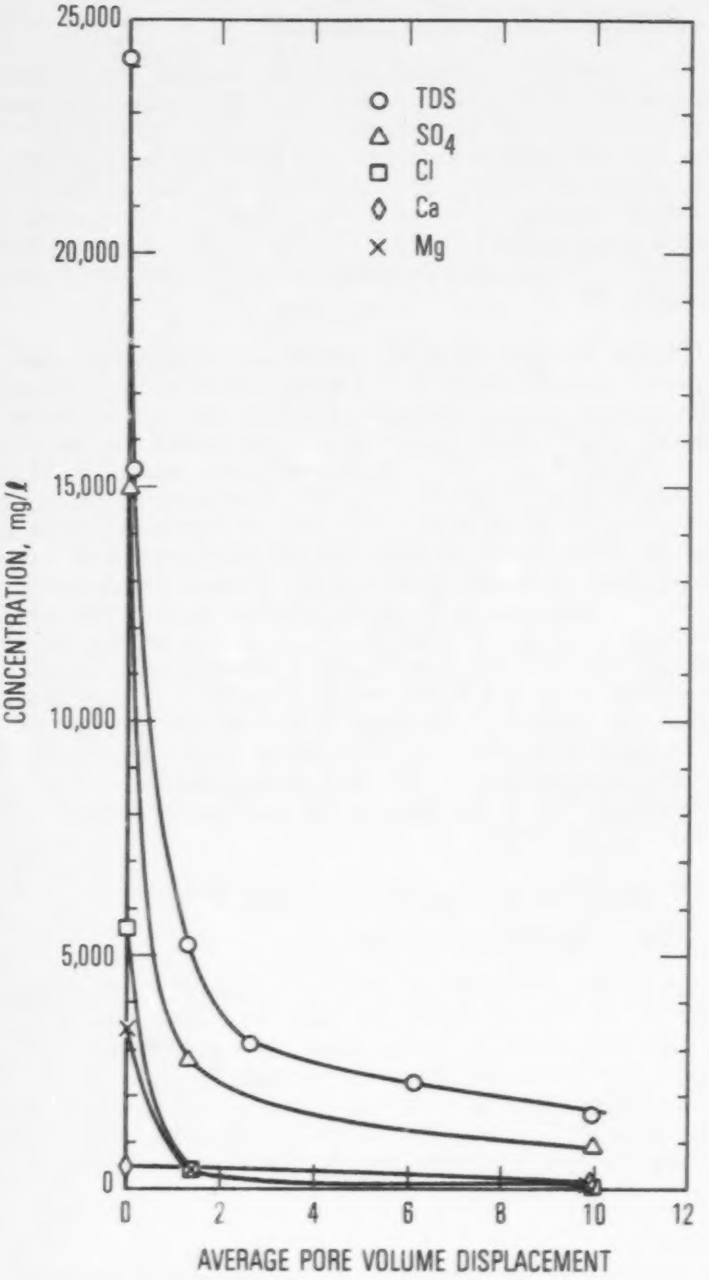

Figure 18. Concentration of major species and TDS in filtrate and leachate of sludge: LG&E Paddy's Run

7.4.3 Assessment of Chemical Data

In Table 21, gypsum solubility ratios* calculated for all of the sludge liquors and leachates are presented. The spread of these ratios is from 0.48 (for the 10th PVD leachate sample from The Paddy's Run sludge) to 1.46 (for the first PVD leachate from the Gulf Scholz sludge), and the mean of the 15 values is 1.04. In view of the spread of the ionic strengths of these liquors and leachates from 0.04 to 3.0, corresponding to a range of sulfate concentrations from 900 to 84,000 mg/ℓ, gypsum saturation is indicated in every case with the possible exception of the Paddy's Run 10th PVD leachate sample.

Table 21 also contains mass and charge balances calculated from the analytical data for each of 15 samples of sludge liquors and leachates. The spread of the calculated mass ratios, given by the sum of the ion concentrations divided by the TDS (corrected for the water of hydration of $CaCl_2 \cdot 2H_2O$), is 0.85 to 1.19, with a mean of 0.97. This indicates that all of the major species present in the analyzed solutions have been accounted for within the accuracy of the measurements. The ionic charge ratio, given by the sum of the equivalent concentrations of cations divided by the sum of the equivalent concentrations of anions, is an even more severe test of the internal consistency of the analytical data. The charge ratios for the 15 samples span a range of from 0.71 to 1.38, with a mean value of 1.08. By a comparison of the three ratios for a given sample, it is possible to identify individual analyses that are questionable. Examination of the analytical results in Tables 17 through 19 for the 15 samples indicates that several of the analyses for calcium may be in error by 10 to 20 percent. However, each of the samples involved had high ionic strength, which makes it difficult to obtain higher accuracy in the analyses for metal ions, and, particularly, trace elements.

7.4.4 Assessment of the Effect of Fly Ash on Trace Element Contents

In Tables 17 through 19, complete chemical analyses for major components and for 10 selected trace elements are reported for the sludge liquors and leachates from the three power plants. In Table 17, analytical results are given for Shawnee sludge filtrate liquor and for leachate samples from leaching tests of both the ash-free sludge and the sludge with 40-wt% fly ash mixture.** Results for both ash-free sludge and sludge containing 30 percent fly ash from the Scholz plant are given in Table 18. The

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* This ratio is defined as the product of the measured calcium and sulfate concentrations divided by the solubility product constant (corrected for the effects of ionic strength.)

** These fly ash percentages represent a dry weight percent of the solids content of the sludge liquor.

TABLE 21. MASS BALANCE, CHARGE BALANCE, AND GYPSUM SOLUBILITY RATIO OF SLUDGE LIQUORS AND LEACHATES

Sample Source	Mass Ratio[a]	Charge Ratio[b]	Ionic Strength	Solubility Ratio[c]
TVA Shawnee Sludge				
Run E Filtrate	1.01	1.29	0.14	0.97
Run F Filtrate	0.88	1.38	0.27	0.85
Run F Leachate (No Fly Ash):				
1st PVD	0.93	1.18	0.12	1.07
6th PVD	1.03	1.02	0.05	0.82
Run F Leachate (40% Fly Ash):				
1st PVD	1.01	0.87	0.12	1.20
7th PVD	0.97	1.03	0.07	1.23
Gulf Scholz Sludge				
Filtrate (No Fly Ash)	0.91	1.29	2.91	1.19
Leachate (No Fly Ash):				
1st PVD	1.01	1.08	0.21	1.46
6th PVD	0.86	1.08	0.09	1.22
Filtrate (30% Fly Ash)	0.90	1.27	3.03	0.91
Leachate (30% Fly Ash):				
1st PVD	0.98	0.98	0.36	1.17
9th PVD	1.17	1.32	0.07	1.36
LG&E Paddy's Run Sludge				
Filtrate	1.19	0.71	0.71	0.86
Leachate:				
1st PVD	0.85	0.92	0.13	0.80
10th PVD	0.91	0.82	0.04	0.48
Average	0.97 (±0.10)	1.08 (±0.20)		1.04 (±0.26)

[a] Mass ratio = Σ all ion concentrations/TDS (corrected for water in $CaCl_2 \cdot 2H_2O$ not lost in drying).

[b] Charge ratio = Σ equivalent concentrations of cations/Σ equivalent concentrations of anions.

[c] Solubility ratio = Measured calcium concentration × measured sulfate concentration/ K_{sp} (solubility product constant corrected for ionic strength).

results for the Paddy's Run plant are given in Table 19 for filtrate and leachate of a sludge containing 12 percent nonsulfur solids.

A comparison of analyses are given in Table 22 for Shawnee lime sludge filtrate liquors from two scrubber test runs in 1976, in which the fly ash was removed ahead of the scrubber and from three runs made early in 1974, in which the fly ash was present in the flue gas. The pH of each of the liquors is in the range of 8 to 9. The analytical results for the startup run of 3/19/74 differ from the others in that the TDS, Na, K, and Mg concentrations are much lower, and the As and Hg levels are much higher than those of any of the other runs. The results of this run have been retained in Table 22, so as to include all of the previous data from the lime scrubber at Shawnee. The Mg and SO_4 concentrations are much higher in the 1976 filtrate as a result of the deliberate addition of MgO with the lime in the scrubbing operation.

Comparisons of trace element concentration levels in samples with and without fly ash can be seen in Table 22. With a single exception, the results for non-fly-ash filtrates (Runs E and F) all are approximately at the level of the lowest of the three samples that contained fly ash or, in several cases, range between the lowest and the median values for the 1974 runs. The single exception is Zn which is appreciably lower in the Run E and Run F filtrates.

Examination of the leachate analytical results in Table 17 for Shawnee Run F ash-free sludge and sludge to which 40-wt% fly ash had been added shows that five trace element concentrations are greater in the sludge with fly ash leachate; four are approximately the same in both leachates; and two trace element concentration levels are higher in the ash-free sludge. Only for B and Se are the differences greater than by a factor of three. However, for As, Hg, and Zn, the levels in the leachate of the sludge with fly ash mixture are higher than those in the Run F ash-free filtrate liquor. Furthermore, the last PVD of leachate show higher Zn concentrations than the first PVD. It is possible that the trace element Zn is incorporated in sulfite or carbonate solid phases, whose solubilities are sufficiently greater at the slightly lower pH of the last leachate samples to release the greater amounts of Zn observed. A similar pattern is observed for the Zn concentrations in the leachates from the Paddy's Run sludge in Table 19. The behavior of As and Hg may also be a consequence of their release from a solid phase during leaching.

No leaching tests were made on the previous (1974) samples of Shawnee lime sludge which contained fly ash; therefore, comparative data were not generated for the leaching of sludge containing fly ash that was scrubbed with the flue gas. Such a comparison can be made of the analytical data for the leachates from the two Scholz sludge samples shown in Table 18. However, the pH range of the double alkali process used at the Gulf Scholz plant is too high to expect to see evidence of acid leaching of fly ash during the scrubbing operation. The high pH of the liquors, ~12,

TABLE 22. COMPARATIVE ANALYTICAL RESULTS FOR SHAWNEE LIME SCRUBBER FILTRATE LIQUORS

Constituent	With Fly Ash[a]			Without Fly Ash[a]	
	3/19/74	5/16/74	6/27/74	8/23/76[b]	9/8/76[c]
pH	9.4	8.8	8.7	8.9	8.0
TDS	2800	8400	9400	5650	10,260[d]
Arsenic	0.15	0.01	0.02	<0.004	0.058
Beryllium	0.026	0.05	<0.002	<0.001	<0.001
Boron	--	--	46	9	76
Cadmium	0.03	0.013	0.11	0.025	0.013
Calcium	660	2420	2520	1450	650
Chromium	0.03	0.02	0.03	0.008	0.011
Copper	0.05	0.04	0.002	<0.003	0.005
Gold	0.01	0.13	0.33	0.010	0.010
Magnesium	24	200	420	220	1730[d]
Mercury	0.07	<0.05	<0.001	<0.00006	<0.00006
Potassium	11	27	28	22	24
Selenium	0.09	1.9	<0.02	0.022	0.078
Sodium	36	109	127	130	137
Zinc	0.01	0.02	0.08	0.002	<0.001
Chloride	1050	4200	4900	1850	1320
Fluoride	1.4	3.0	3.3	1.3	1.9
Sulfate	900	1250	800	1100	4500[d]

[a] Concentrations in mg/ℓ, as appropriate.

[b] Designated in Shawnee Scrubber Test Program as Run E.

[c] Designated in Shawnee Scrubber Test Program as Run F.

[d] Magnesium added to lime to evaluate absorbent efficiency.

is the cause of the virtual absence of Mg, which was precipitated as the hydroxide and only begins to reappear in the leachates after elution has lowered the pH to below 9. Examination of the data of Table 18 shows that, of the trace elements listed, only As and Cr are found in higher concentrations in the leachate from the sample that contained fly ash. The lower pH of the ninth PVD leachate sample from the Scholz sludge containing fly ash may also be responsible for the higher concentrations of these two elements. It is noteworthy that the fluoride concentrations are higher in the liquors and leachates of the ash-free sludge.

7.5 RESULTS OF LEACHING FLY ASH AT CONTROLLED pH

Fly ash obtained from TVA Shawnee was mixed in the proportion of two parts mechanically separated ash to one part electrostatically separated ash. To this mixture, dilute $HC\ell$ was added as required to maintain a constant pH, using a glass electrode as an indicator. Two acid equilibrations, one at pH 4.0 and the other at pH 7.1, were continued until the pH remained constant and then were allowed to stand with constant stirring for 24 hr.

The concentrations of trace elements measured in the solutions at pH 4 and pH 7 are shown in Table 23. Only the concentrations of Cd, Cu, and Pb appeared to be significantly higher in the sample at pH4 than in the sample at pH 7. Selenium was found in higher concentrations in the sample at pH 7 than in the sample at pH 4. Of all the trace element concentrations measured in the fly ash leaching tests, only the concentrations of Cd, Cu, and Pb in the sample at pH 4 were found to be significantly higher than the values for these elements measured in the sludge with fly ash leaching tests. The concentration levels of all other trace elements in the fly ash leaching were comparable to those in the sludge with fly ash leachate except for the concentrations of As in the fly ash leachates, which were lower than those measured in the sludge with fly ash leaching tests.

7.6 RESULTS OF SOLIDS ANALYSES

Dry sludges from three power plants were analyzed for their major components. The results of these analyses are shown in Table 24. The samples of Gulf Scholz sludge that was received from A. D. Little, Inc. were accompanied by the analytical results for the same sample. These data have been included in Table 24. Comparison shows good agreement between the analytical results from both laboratories. It may be noted that material balances are well within 5 percent for all three sludges.

Each of the sludge solids contained greater than 15 percent gypsum. Neither the Scholz nor the Shawnee sample contained a significant amount of fly ash, but the Paddy's Run sludge contained about 12 percent ash and, in addition, about 3.5 percent carbon. The Scholz sludge also

TABLE 23. TRACE ELEMENTS LEACHED FROM SHAWNEE FLY ASH AT CONTROLLED pH[a, b]

pH	4.0	7.1
Arsenic	0.039	0.058
Beryllium	<0.001	<0.001
Cadmium	0.036	0.009
Chromium	0.006	0.009
Copper	0.036	0.003
Lead	0.022	<0.005
Mercury	0.00012	0.00015
Selenium	0.006	0.026
Sodium	10	10
Zinc	0.01	0.005

[a] Concentrations in mg/ℓ, as appropriate.

[b] Shawnee fly ash mixture of two parts mechanically separated ash and one part electrostatically separated ash, September 1976.

TABLE 24. COMPOSITION OF DRY SOLID SLUDGE FROM THREE POWER PLANTS, IN WEIGHT PERCENT

Component	TVA Shawnee, Lime (Run F)	LG&E Paddy's Run, Carbide Lime	Gulf Scholz, Double Alkali	Gulf Scholz (analysis by A. D. Little, Inc.)
$CaSO_4$[a]	19.4	15.1	15.3	–
$CaSO_4$[b]	–	–	–	13.9
$CaSO_3$[c]	69.2	37.4	68.1	68.1
$CaCO_3$	10.3	29.5	10.1	8.2[d]
Insolubles[e] in HCl	–	15.9[e]	–	–
Na_2SO_4[f]	–	–	3.7	3.5
Total	98.9	97.9	97.2	93.7

[a] Expressed as $CaSO_4 \cdot 2\ H_2O$.

[b] Expressed as $CaSO_4 \cdot 1/2\ H_2O$.

[c] Expressed as $CaSO_3 \cdot 1/2\ H_2O$.

[d] Calculated from excess Ca.

[e] Contained 3.5 percent carbon (loss on ignition [LOI]).

[f] Calculated from Na.

contained about 4 percent sodium salts from the double alkali process. Residual calcium carbonate amounted to about 10 percent for the Shawnee and Scholz sludges and almost 30 percent for the Paddy's Run sludge.

7.7 SUMMARY AND CONCLUSIONS

The results of the fly ash equilibration and leaching tests show that low pH scrubbing of fly ash could produce higher levels of several trace elements than is produced in high pH sludge with fly ash liquors. Of the nine trace element concentrations measured, three were higher in the low pH sample; one was higher in the high pH sample; and five were not significantly different in the two samples. Moreover, the data show that the concentrations of trace metals in fly ash leachate are essentially equivalent to the concentration of these metals in sludge with fly ash leachate having the same pH.

A comparison of trace element concentrations in the filtrate liquors of Shawnee ash-free lime sludge and sludge obtained by scrubbing flue gas containing fly ash show that only one element, zinc, had a significantly lower concentration in the liquor from the ash-free sludge. For the other eight elements, the concentrations in the ash-free sludge liquor were comparable either to the lowest levels or to the median levels observed for the liquors from sludge containing fly ash. Similarly, for the leachates from the two Scholz plant sludges, one ash-free and the other containing fly ash, only two trace element concentrations were significantly higher in the leachate from sludge containing fly ash. Leachates of the ash-free Shawnee lime sludge and the sludge mixed with 40-wt% fly ash showed comparable concentration levels for all except one trace element. From these data, it is concluded that the presence of fly ash in a sludge will cause significantly increased concentrations of only a few trace metals in the liquor or leachate by as much as a factor of 10 over concentrations in the liquor or leachate of a sludge containing no fly ash.

Examination of the solid phases of each of the ash-free sludges with the SEM showed the presence of some fly ash particles. It is probable that the finest fly ash particles, i.e., those with the largest relative surface area and therefore the highest leachability, are carried past the separators by the flue gas and are collected in the scrubber. The trace elements found in the liquors of ash-free sludge may be explained by the presence of minor quantities of fly ash. Since the finest fly ash particles can remain suspended in the liquors and leachates and pass through the pores of the filters used, it is possible that these suspended particles are subsequently analyzed, and not all the reported concentration levels of trace elements represent dissolved species. Additionally, other input ingredients such as lime, limestone, and magnesium oxide may contribute a low level of trace elements of the liquor. It is concluded from these data that removal of fly ash ahead of the scrubber does not eliminate the trace elements from the sludge liquors and leachates, but the concentration levels of some trace elements may be significantly reduced.

SECTION VIII

ANALYSIS OF FORCED OXIDATION GYPSUM

8.1 BACKGROUND OF GYPSUM FROM FORCED OXIDATION OF RTP PILOT PLANT LIMESTONE SCRUBBER SLUDGE

In the U.S. Environmental Protection Agency (EPA) Emissions/ Effluent Technology Branch, Research Triangle Park (RTP), North Carolina, R. Borgwardt has been conducting pilot-plant-scale experiments evaluating the forced oxidation of sulfite sludges from the limestone and lime scrubbing of SO_2 from flue gas. The experiments were designed to determine limestone utilization, oxidation efficiency, settling rates and bulk densities of the gypsum product. The pilot plant system consisted of a first-stage spray tower and a second-stage turbulent contact absorber (TCA) loop (Figures 19 and 20). The first-stage loop contained a holding tank equipped for air sparging to bring about complete oxidation of the sulfite. A portion of the oxidized slurry was bled off to a vacuum drum filter. Burner combustion products simulated flue gas with SO_2 and HCl being introduced into the gas stream. Fly ash was introduced, when desired, with the limestone in the second-stage loop.

To augment the numerous chemical analyses and physical property measurements being made at RTP and reported by Borgwardt References 14 and 19, Aerospace conducted additional characterization tests on filter cake and slurries from the first- and second-stage loops of samples from two runs utilizing limestone scrubbing, one with and the other without added fly ash. Scanning electron microscope (SEM) and x-ray examinations were made of crystalline phases, and wet chemical analyses were made for major constituents of both the solid and liquid phases. Also, the leaching characteristics of the solids were determined. Physical properties including bulk densities, compressive strengths, and permeabilities were also measured, and cost estimates of gypsum production by forced oxidation were made.

8.2 CHEMICAL AND LEACHING CHARACTERISTICS

SEM, x-ray, and wet chemical analyses were made of the filtered solids and solids from the first- and second-stage slurries. All the

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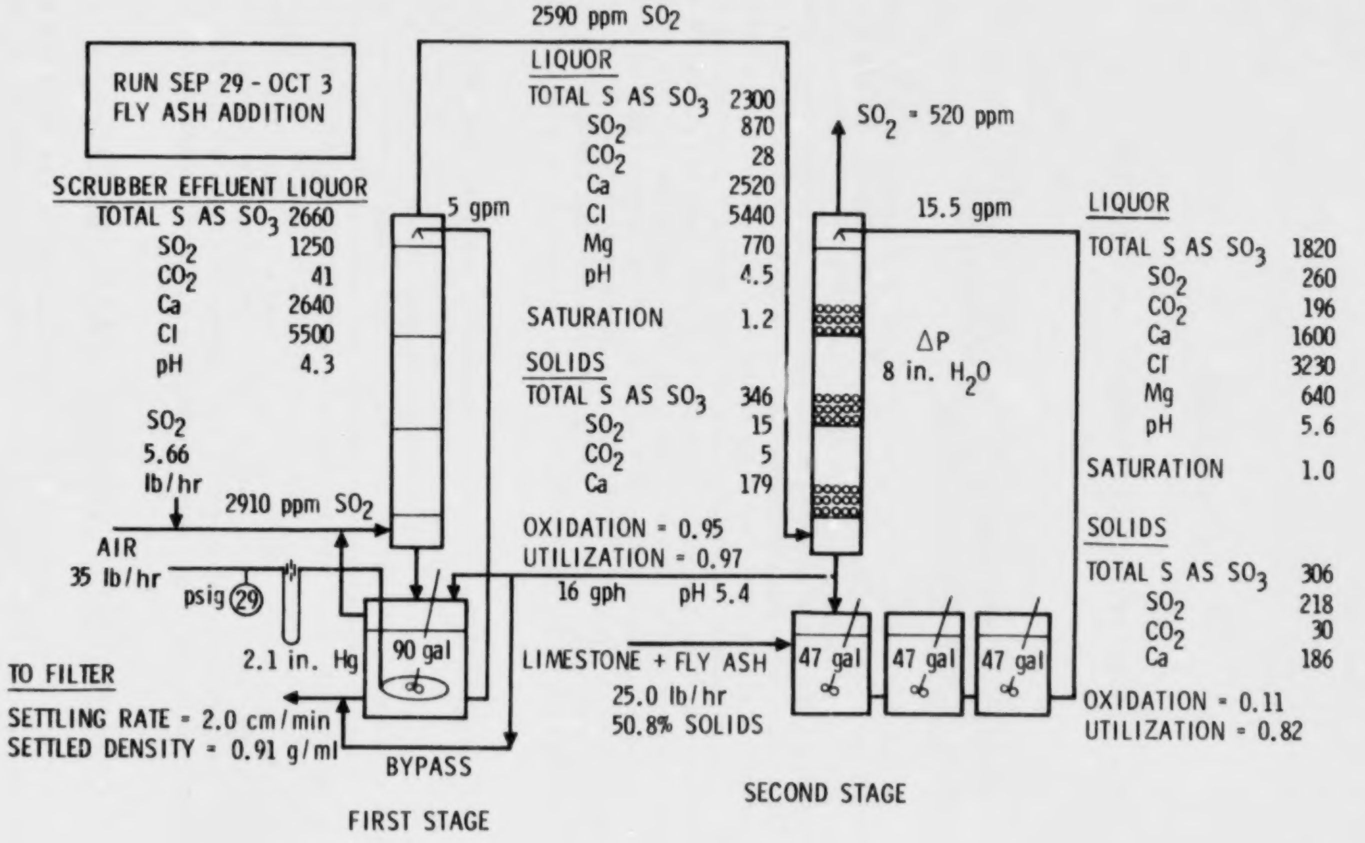
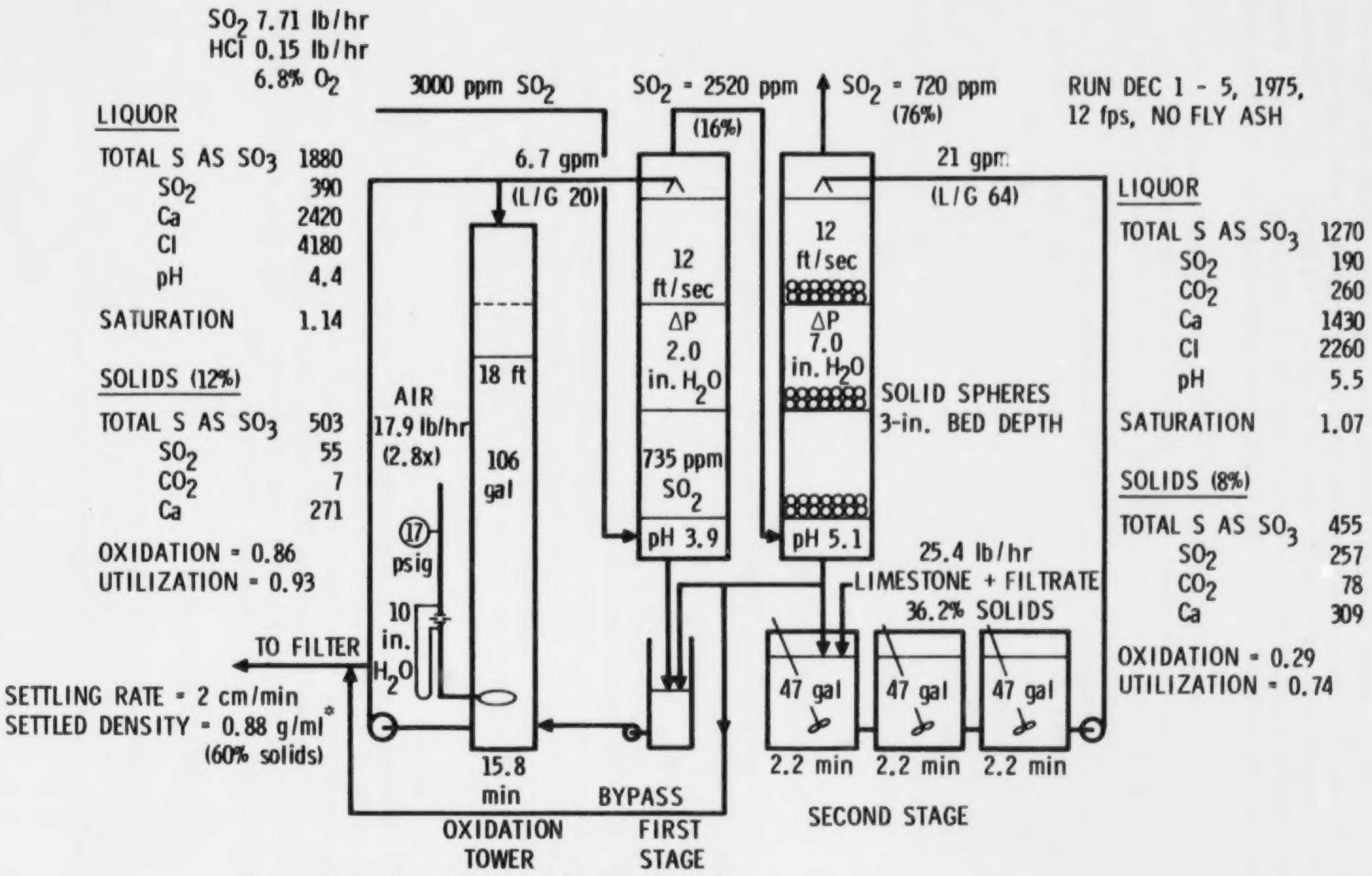

RUN SEP 29 - OCT 3
FLY ASH ADDITION
SCRUBBER EFFLUENT LIQUOR
TOTAL S AS SO_3 2660
SO_2 1250
CO_2 41
Ca 2640
Cl 5500
pH 4.3
SO_2
5.66
lb/hr
2910 ppm SO_2
AIR
35 lb/hr
psig ㉙
2.1 in. Hg
90 gal
TO FILTER
SETTLING RATE = 2.0 cm/min
SETTLED DENSITY = 0.91 g/ml
BYPASS
FIRST STAGE
5 gpm
2590 ppm SO_2
LIQUOR
TOTAL S AS SO_3 2300
SO_2 870
CO_2 28
Ca 2520
Cl 5440
Mg 770
pH 4.5
SATURATION 1.2
SOLIDS
TOTAL S AS SO_3 346
SO_2 15
CO_2 5
Ca 179
OXIDATION = 0.95
UTILIZATION = 0.97
16 gph
pH 5.4
LIMESTONE + FLY ASH
25.0 lb/hr
50.8% SOLIDS
SO_2 = 520 ppm
15.5 gpm
ΔP
8 in. H_2O
47 gal
47 gal
47 gal
SECOND STAGE
LIQUOR
TOTAL S AS SO_3 1820
SO_2 260
CO_2 196
Ca 1600
Cl 3230
Mg 640
pH 5.6
SATURATION 1.0
SOLIDS
TOTAL S AS SO_3 306
SO_2 218
CO_2 30
Ca 186
OXIDATION = 0.11
UTILIZATION = 0.82

Figure 19. EPA pilot plant forced oxidation system tests with fly ash


SO_2 7.71 lb/hr
HCl 0.15 lb/hr
6.8% O_2
LIQUOR
TOTAL S AS SO_3 1880
SO_2 390
Ca 2420
Cl 4180
pH 4.4
SATURATION 1.14
SOLIDS (12%)
TOTAL S AS SO_3 503
SO_2 55
CO_2 7
Ca 271
OXIDATION = 0.86
UTILIZATION = 0.93
TO FILTER
SETTLING RATE = 2 cm/min
SETTLED DENSITY = 0.88 g/ml*
(60% solids)
3000 ppm SO_2
6.7 gpm
(L/G 20)
AIR
17.9 lb/hr
(2.8x)
⑰
psig
10
in.
H_2O
18 ft
106
gal
15.8
min
OXIDATION
TOWER
SO_2 = 2520 ppm
(16%)
12
ft/sec
ΔP
2.0
in. H_2O
735 ppm
SO_2
pH 3.9
BYPASS
FIRST
STAGE
SO_2 = 720 ppm
(76%)
12
ft/sec
ΔP
7.0
in. H_2O
pH 5.1
SOLID SPHERES
3-in. BED DEPTH
21 gpm
(L/G 64)
25.4 lb/hr
LIMESTONE + FILTRATE
36.2% SOLIDS
47 gal
47 gal
47 gal
2.2 min
2.2 min
2.2 min
SECOND STAGE
RUN DEC 1 - 5, 1975,
12 fps, NO FLY ASH
LIQUOR
TOTAL S AS SO_3 1270
SO_2 190
CO_2 260
Ca 1430
Cl 2260
pH 5.5
SATURATION 1.07
SOLIDS (8%)
TOTAL S AS SO_3 455
SO_2 257
CO_2 78
Ca 309
OXIDATION = 0.29
UTILIZATION = 0.74

* Grams dry solid per ml final settled volume.

Figure 20. EPA pilot plant forced oxidation system tests without fly ash

measurements are in substantive agreement with each other as to the composition of the solids. The second-stage slurry contained primarily hydrated calcium sulfite, $CaSO_3 \cdot 1/2H_2O$, with a small amount of gypsum. Both the first-stage slurry solids and the filtered solids were primarily gypsum with small amounts (<1 percent and <6 percent, respectively) of $CaSO_3 \cdot 1/2H_2O$. The filtered solids contained more $CaSO_3 \cdot 1/2H_2O$ than did the first-stage slurry. However, the latter is not indicative of the basic characteristics of the process.

The presence of $CaSO_3 \cdot 1/2H_2O$ in the filtered solids, in view of its virtual absence from the first-stage slurry, was an unprogrammed plumbing modification whereby a portion of the second-stage slurry was sent directly to the filter, bypassing the first-stage loop as a means of controlling the percent solids in the second stage. SEM examination of filtered solids from RTP tests of March 1-5, 1976, which were definitely known to have the first-stage by-pass, also showed some $CaSO_3 \cdot 1/2H_2O$, as expected, and comparable tests of March 15-19, 1976, where the bypass condition was corrected, showed only gypsum. As a result of this plumbing configuration, the effect of calcium sulfite mixed with gypsum was established, as well as the primary objectives of determining gypsum properties. The characteristics of the gypsum-calcium sulfite combination normally would not have been determined.

8.2.1 X-Ray Diffraction Measurements

The crystalline phase of gypsum, $CaSO_4 \cdot 2H_2O$ was identified in each sample of solids from the RTP pilot plant. Although precise quantitative analyses are not possible with x-ray measurements, the major and minor components of each of the samples were identified and are shown in Table 25. Gypsum was the major crystalline phase of both first-stage slurry and filtered solids and was a minor phase of the second-stage slurry. Calcium sulfite hemihydrate was the major crystalline phase of the second-stage slurry and was a minor phase of the filtered solids. The extent to which it could normally be expected was not determined because of the nonstandard plumbing configuration. Data included in Table 25 for samples removed from the columns at the conclusion of leaching tests are discussed in Section 8.2.4.

As shown in Table 25, x-ray diffraction measurements verified that each of the samples dried in ambient air contained gypsum. For those samples dried at 90°C at atmospheric pressure or at 50°C under vacuum, some or all of the gypsum was converted to the hemihydrate $CaSO_4 \cdot 1/2H_2O$. In one case, there was an indication that some hemihydrate was formed during ambient air drying. In contrast, the hemihydrate of calcium sulfite appears to be unaffected by prolonged vacuum drying at 50°C.

8.2.2 SEM Measurements

SEM photography confirmed the presence of gypsum in the filtered solids and the first-stage solids (Figures 21 through 26). The first-stage slurry solids contained only gypsum crystals, while the filtered solids

TABLE 25. CRYSTALLINE PHASES IN RTP OXIDIZED SLUDGES IDENTIFIED BY X-RAY DIFFRACTION

Source of Sample	Sample Treatment	Major Constituent
Sampled 9/30/75, Contained Fly Ash:		
Filtered Solids	Dried in air @ 90°F	$CaSO_4 \cdot 1/2H_2O$
Filtered Solids	Ambient air dried	$CaSO_4 \cdot 2H_2O^a$
1st Stage Slurry Solids	Ambient air dried	$CaSO_4 \cdot 2H_2O$
2nd Stage Slurry Solids	Ambient air dried	$CaSO_3 \cdot 1/2H_2O$
Filtered Solids	From leachate column Dried in ambient air	$CaSO_4 \cdot 2H_2O^a$
1st Stage Slurry Solids	From leachate column Dried in ambient air	$CaSO_4 \cdot 2H_2O$
2nd Stage Slurry Solids	From leachate column Dried in ambient air	$CaSO_3 \cdot 1/2H_2O$
Sampled 12/4/75, Contained No Fly Ash:		
Filtered Solids	Ambient air dried	$CaSO_4 \cdot 2H_2O^a$
Filtered Solids	Vacuum dried at 50°F	$CaSO_4 \cdot 1/2H_2O$
1st Stage Slurry Solids	Ambient air dried	$CaSO_4 \cdot 2H_2O^a$
1st Stage Slurry Solids	Vacuum dried at 50°F	$CaSO_4 \cdot 1/2H_2O$
2nd Stage Slurry	Vacuum dried at 50°F	$CaSO_3 \cdot 1/2H_2O$

[a] Small quantities of $CaSO_3 \cdot 1/2H_2O$ in sample.

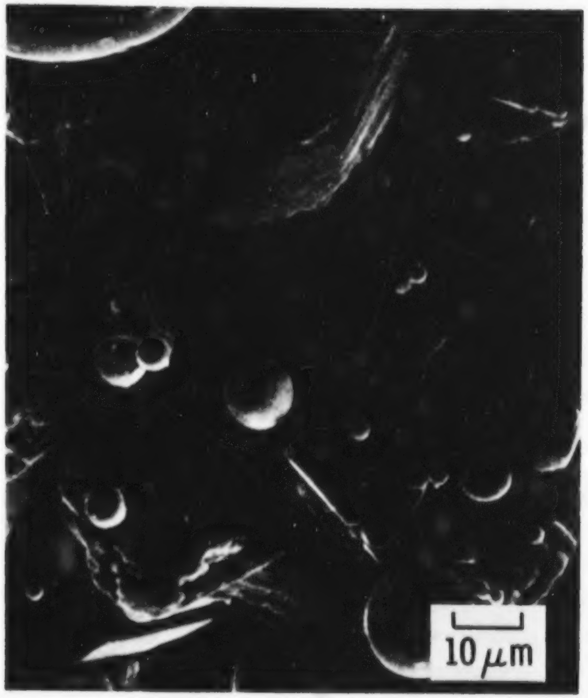


Figure 21. RTP first-stage slurry solids containing predominantly gypsum, fly ash, and small quantities of calcium sulfite (sampled 1/30/75), X1000

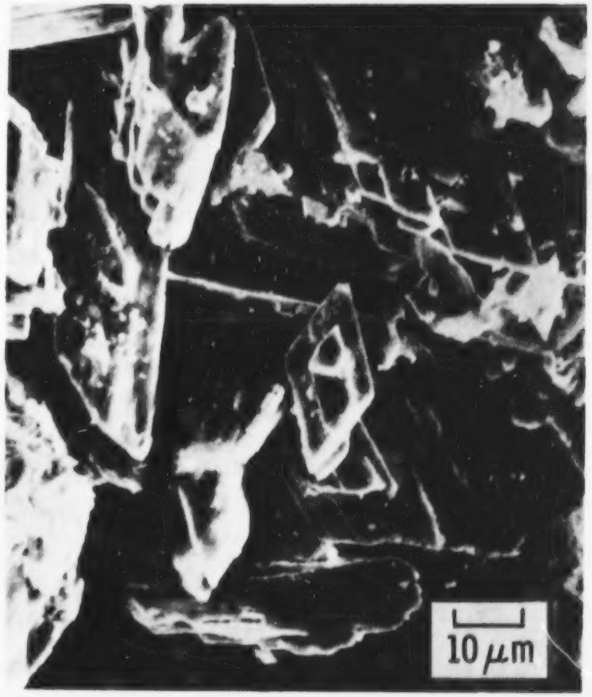


Figure 22. RTP first-stage slurry solids containing predominantly gypsum and small quantities of calcium sulfite (sampled 12/4/75), X1000

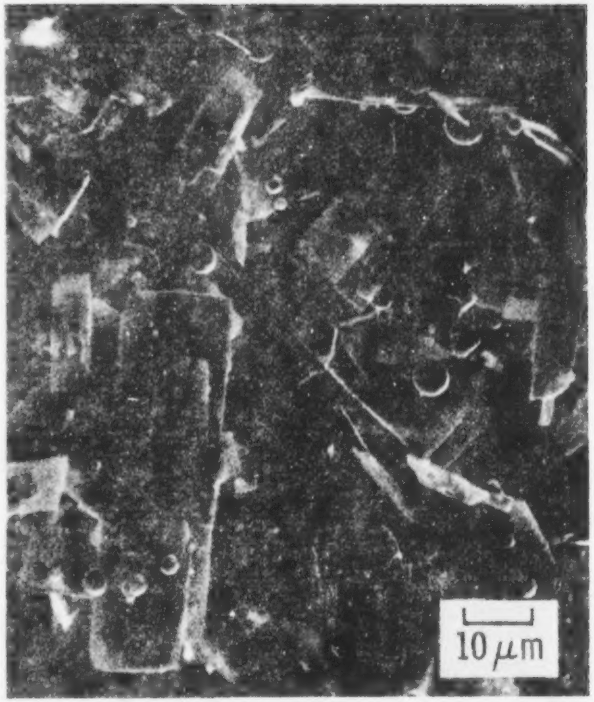


Figure 23. RTP second-stage slurry solids containing predominantly calcium sulfite and fly ash (sampled 9/30/75), X1000

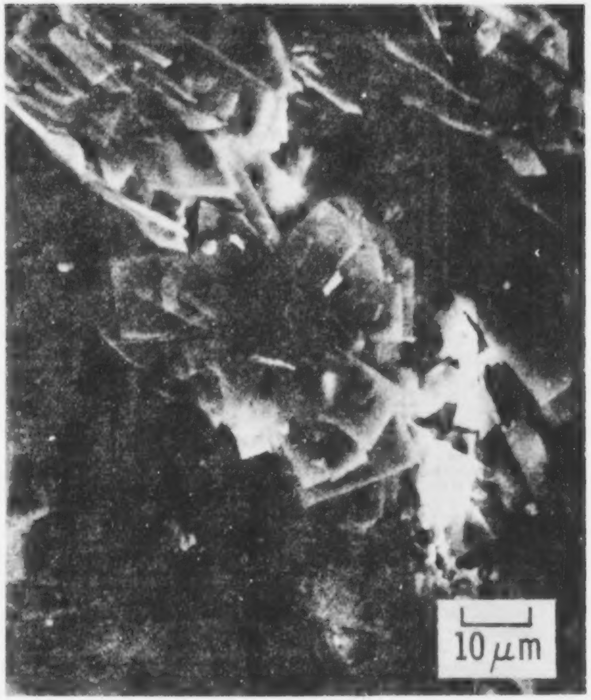


Figure 24. RTP second-stage slurry solids containing predominantly calcium sulfite (sampled 12/4/75), X1000

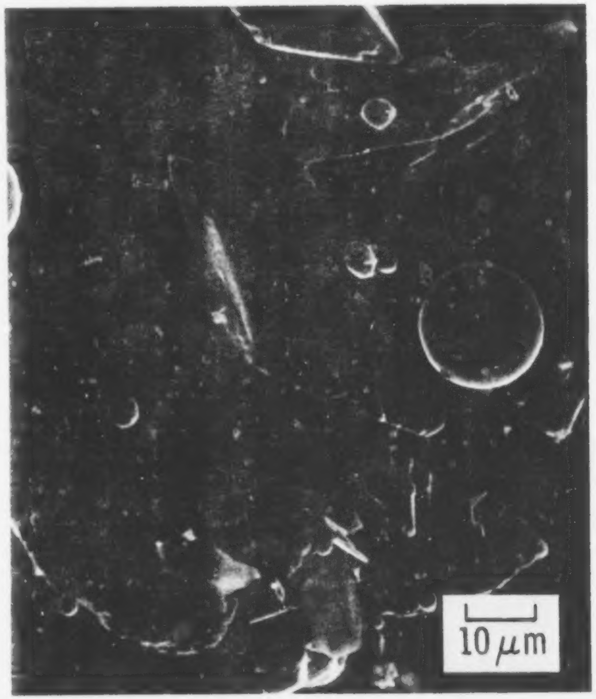


Figure 25. RTP filtered solids containing gypsum, fly ash, and approximately 5-percent calcium sulfite (sampled 9/30/75), X1000

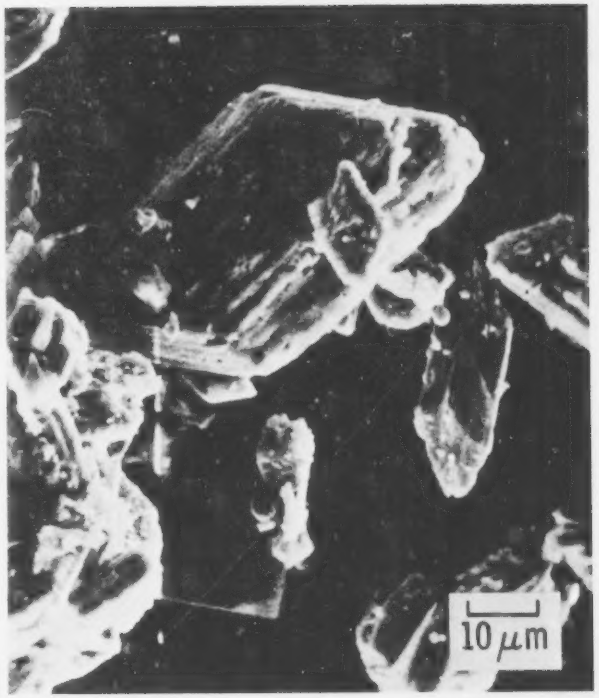


Figure 26. RTP filtered solids containing gypsum and approximately 5-percent calcium sulfite, X1000

contained mostly gypsum with a small amount of calcium sulfite hemihydrate. The second-stage slurry solids contained mostly calcium sulfite hemihydrate with only a small amount of either gypsum or calcium carbonate. Fly ash was evident as spherical particles in those samples (9/30/75) where fly ash was included in the process.

8.2.3 Wet Chemical Analyses

The chemical analyses of the dried sludge solids are shown in Table 26. As a result of the sludge being oven-dried prior to analysis, the gypsum was converted to the hemihydrate; therefore, the calcium sulfate analyses are reported as $CaSO_4 \cdot 1/2\,H_2O$.

As observed in the SEM photographs, the filtered solids and the first-stage solids were predominantly sulfate and the second stage primarily calcium sulfite. Although the filtered solids contained primarily the gypsum phase of the sulfate, approximately 5 percent calcium sulfite was observed in each of the two samples analyzed. The presence of sulfite was not due to incomplete oxidation in the first-stage loop but was determined to be the result of an unscheduled modification of the plumbing whereby a portion of the second-stage slurry bypassed the first-stage loop.

The quantitative results of the wet chemical analyses verified conclusively that complete oxidation of calcium sulfite to gypsum was achieved in the first-stage loop.

Calcium, magnesium, chloride, sulfate and total dissolved solids (TDS) were reported for the filtrates from both samplings. The results are shown in Table 27. Mass and charge balance calculations were also included and the results expressed as ratios in Table 27. The close proximity to unity of these ratios corroborates the results of the chemical analyses. Since the analytical data appear to indicate saturation of the filtrates with gypsum, a solubility ratio was also determined. It was defined as the product of the measured calcium and sulfate ion concentrations divided by the theoretical solubility product constant corrected for the effect of ionic strength. These ratios also are approximately unity, thus verifying gypsum saturation.

8.2.4 Leaching Test Results

Leaching test results of RTP limestone-scrubbed FGC gypsum wastes from sludge samples of September 30, 1975 (with fly ash) and December 4, 1975 (without fly ash) are outlined in Table 27.

On the basis of the drying conditions used in the TDS determination, the $CaCl_2 \cdot 2H_2O$ in the solids was not dehydrated when the sample was brought to constant weight; therefore, a correction was applied to reduce the TDS by the moles of H_2O in the hydrated $CaCl_2$.

The results for the filtered solids and first-stage slurry solids show that, after two to three pore volumes of water have passed through the

TABLE 26. COMPOSITION OF RTP OXIDIZED SLUDGE BY WET CHEMICAL ANALYSIS

Sample Designation	Total Solids (% of Slurry)	Composition of Solids, Percent by Weight, Dry			
		Fly Ash	$CaSO_4 \cdot 1/2\ H_2O^a$	$CaSO_3 \cdot 1/2\ H_2O$	$CaCO_3$
Sampled 9/30/75, Contained Fly Ash					
First-Stage Slurry	11.3	40.0	62.5	<0.5	<0.5
Second-Stage Slurry	12.4	38.4	7.8	41.4	11.4
Filtered Solids	64.9	38.6	52.7	5.7	4.9
Sampled 12/4/75, Contained No Fly Ash					
First-Stage Slurry	----[b]	----	94.6	0.7	8.0
Second-Stage Slurry	----	----	11.8	51.8	37.0
Filtered Solids	----	----	86.4	9.5	----

[a] Drying process converted gypsum to $CaSO_4 \cdot 1/2\ H_2O$.

[b] ---- Not determined.

TABLE 27. ANALYSIS OF LEACHATES AND FILTRATES OF RTP FORCED OXIDATION SAMPLES

Sample and Date	Contained Fly Ash	No. of PVD	Concentration, mg/ℓ								Ionic Strength	Solubility Product Ratio[d]
			TDS	TDS Corrected[a]	Σ^b	η^c	Ca	SO_4	Cl	Mg		
First-Stage Slurry Solids, 9/30/75	Yes	0.7	6820	5840	5140	0.88	1300	1540	2000	300	0.15	1.16
		26.4	2180	3140	2130	0.99	550	1500	80	0.3	0.08	1.19
First-Stage Slurry Solids, 12/4/75	No	1.0	5860	4775	5110	1.07	1280	1450	2160	220	0.14	1.12
		10.3	2160	2120	1620	0.76	540	1000	80	0.04	0.05	0.92
Second-Stage Slurry Solids, 9/30/75	Yes	0.3	6770	5855	5270	0.90	950	1910	1870	540	0.16	0.97
		9.6	300	270	310	1.14	120	150	40	0.3	0.01	0.08[e]
Second-Stage Slurry Solids, 12/4/75	No	0.9	5070	4290	4290	1.00	1080	1500	1530	180	0.12	1.17
		22.1	330	300	380	1.27	100	220	60	0.3	0.01	0.10[e]
Filtered Solids, 9/30/75	Yes	0.6	7100	6010	5470	0.91	1220	1600	2220	430	0.16	1.03
		11.1	2190	2130	2065	0.97	560	1400	90	15	0.06	1.13
Filtered Solids, 12/4/75	No	0.5	10100	8100	7940	0.98	2170	1250	4040	480	0.23	0.94
		14.4	2310	2260	2100	0.93	500	1500	100	0.2	0.06	1.11
Filtrate, 9/30/75	Yes	--	9230	7595	7290	0.96	1420	1800	3330	740	0.22	0.96
Filtrate, 12/4/75	No	--	10490	8515	7750	0.91	2200	1130	3930	440	0.23	0.89

[a] Measured TDS corrected for $2H_2O$ in $CaCl_2 \cdot 2H_2O$.

[b] Σ = sum of Ca, SO_4, Cl, and Mg ions.

[c] Mass ratio: Σ/TDS (corrected.

[d] $(Ca) \times (SO_4)/K_{CaSO_4}$ with K_{CaSO_4} corrected for ionic strength.

[e] K_{CaCO_3} was used.

samples, gypsum, the principal ingredient of both materials, was being dissolved and produced a leachate that was saturated with calcium and sulfate ions.

Each one of the samples of Table 27 was saturated with gypsum, except for two samples of solids from the second-stage slurry at 10 and 22 pore volume displacements (PVD) whereby the gypsum supply had been essentially depleted. These two were saturated with $CaSO_3$. From this point on, the calcium was supplied by the dissolution of hydrated calcium sulfite, although the anions found in the leachate were sulfate because of the rapid oxidation of sulfite ions.

The ratios of the products of the calcium and sulfate molar concentrations to the estimated solubility product constants (corrected for the ionic strength) have been tabulated in the last column of Table 27. It is shown that these ratios were virtually constant and ranged between 0.9 and 1.2. For the two second-stage slurry samples, the solubility product constant of $CaSO_3$ was used. In these two cases, the low values are attributed to very small amounts of residual gypsum in the beds which were still contributing sulfate to the leachates.

In assessing the overall material balance at a PVD of less than 1.0, i.e., TDS versus the summation of the Ca, SO_4, Cl, and Mg ions, it is apparent that considerably better agreement was obtained with those samples without fly ash than those that had fly ash in the scrubber slurry. This indicates that the major species were covered by Ca, SO_4, Cl, and Mg for the no-fly-ash case, whereas some significant additional constituents were probably leached when fly ash was present. It is also apparent that, after many PVD (>10), the concentration of the major species was virtually the same whether or not fly ash was initially present.

The concentrations of TDS and major constituents in leachate from the first-stage slurry solids are plotted against pore volume displacement in Figure 27.

In both samples, the TDS in the leachates reached the same minimum gypsum (saturation) value after about three PVD. The value was unchanged even when the leaching was continued until more than 30 pore volumes had been displaced. The concentrations of magnesium and chloride were reduced as leaching progressed, but sulfate remained relatively constant and calcium was only partially removed, as shown in Table 27. The computed solubility ratios also supported the fact that each of the leachate samples was saturated with gypsum. During leaching, the soluble magnesium and calcium chlorides were washed out of the bed with the residual liquor leaving the crystalline gypsum to saturate the leaching water. The ionic strength decreased as the chlorides were removed, thus reducing the solubility of gypsum.

The results of leaching tests for the filtered solids were similar to those for the first-stage slurries (Figure 28). The TDS leveled out at the same saturation value of about 2200 mg/ℓ.

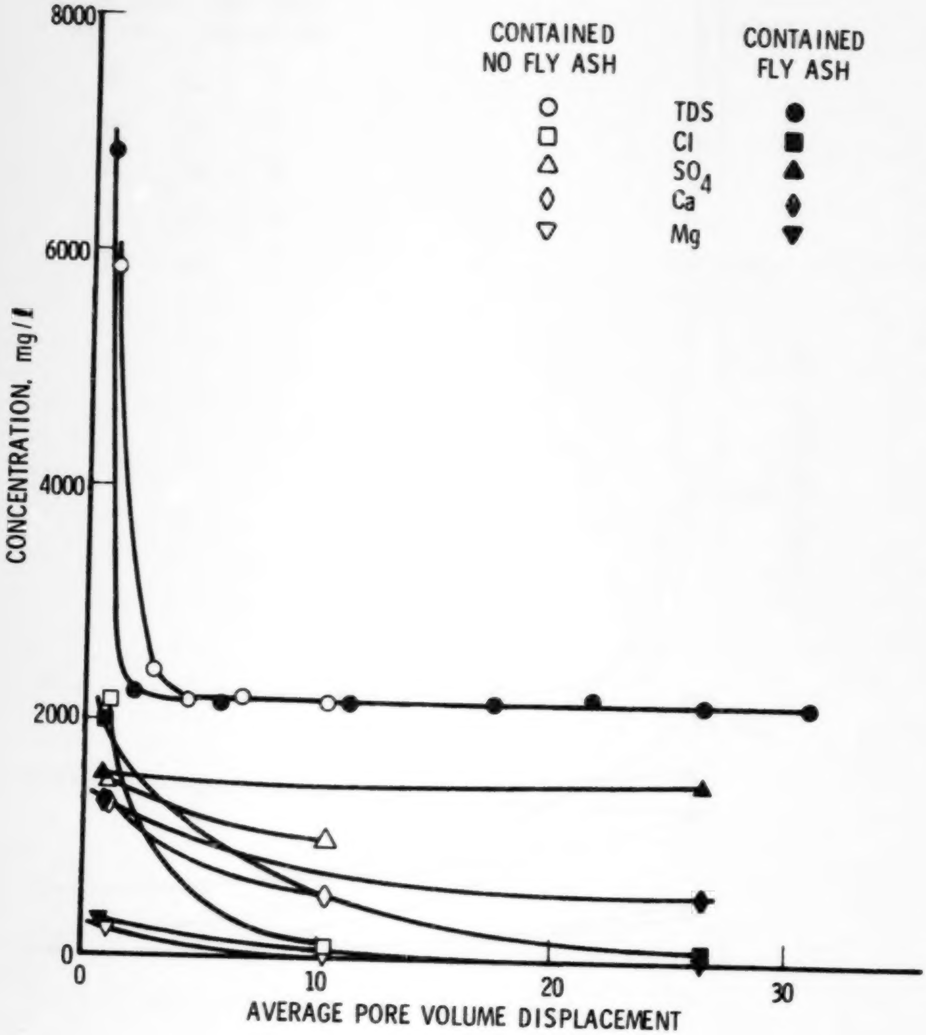


Figure 27. Concentration of major species in leachate of first-stage slurry solids of RTP oxidized sludges

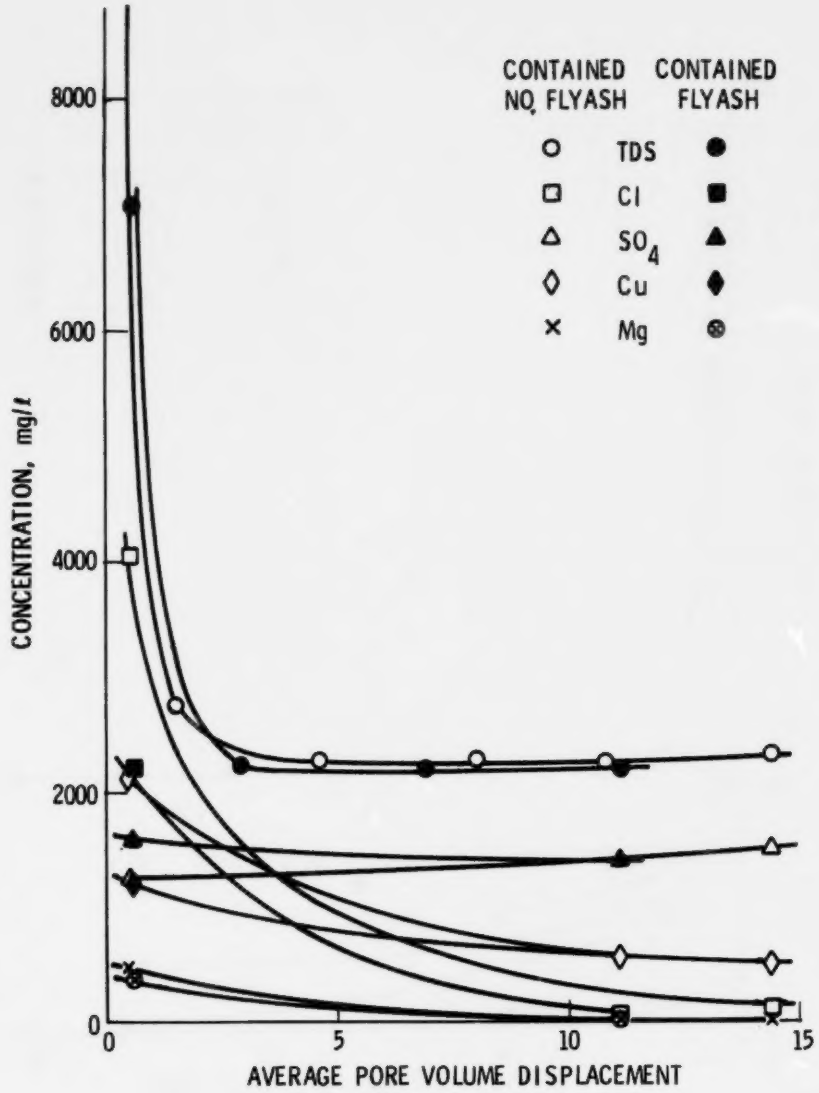


Figure 28. Concentration of major species in leachate from filtered solids of RTP oxidized sludges

It is apparent from the plots of Figure 29 and from the data of Table 27 that the leachate characteristics of the second-stage slurry solids illustrate the different composition of the solids. The same initial pattern of changing TDS with PVD that was observed for the first-stage and filtered solids samples only persists to about five pore volumes. The TDS concentrations (Figure 29), particularly the one for the sample that contained no fly ash, began to level off at the gypsum saturation content of about 2200 mg/ℓ and then decreased to about 300 mg/ℓ when 20 pore volumes were displaced. The sulfate concentrations in the final leachate samples from the second-stage slurries were about 1/10 of the amount in the final leachates of the filtered solids or the first-stage slurries. Therefore, the solubility ratios for these leachate samples are approximately 0.1, as shown in Table 27 and appear to correspond to saturation of the leachate with calcium sulfite hemihydrate.

The inflection points on the TDS curves for the solids from the second-stage slurry solids correspond to the gypsum being depleted. Initially, the available gypsum in the leachate was 8 and 12 percent, with and without fly ash, respectively (Table 26), and was ultimately depleted, leaving only calcium sulfite hemihydrate. This was confirmed, as shown in Table 25, by x-ray diffraction measurements on the leachate bed solids made at the conclusion of the leaching tests.

8.3 PHYSICAL CHARACTERISTICS

Measurements were made of permeability coefficients, void fraction, water retention, unconfined compressive strength, and load-bearing strength of fly-ash-free gypsum, calcium sulfite, and gypsum mixed with 5 to 10 percent calcium sulfite. The effects of fly ash on the properties of the various materials were also determined.

8.3.1 Permeability Coefficients

Permeability coefficients of about 1×10^{-4} cm/sec were reported for all the samples (Table 28). These values were determined for beds that were constructed by loading columns with slurries of the solids and allowing the solids to settle and drain. The lowest value of 5×10^{-5} cm/sec was obtained for a bed that was prepared by "rodding" the slurry during the initial drainage. These results indicate that the second-stage slurry solids, which are primarily calcium sulfite hemihydrates, showed slightly lower permeability coefficients than the samples which were predominantly gypsum.

8.3.2 Density

Samples were prepared by casting slurries in cylindrical containers with perforated bottoms and allowing the settled and drained samples to dry for several days at ambient temperature until the samples were capable of maintaining structural integrity. After weighing, the samples were oven-dried at 50°C to obtain moisture contents. From these measurements and

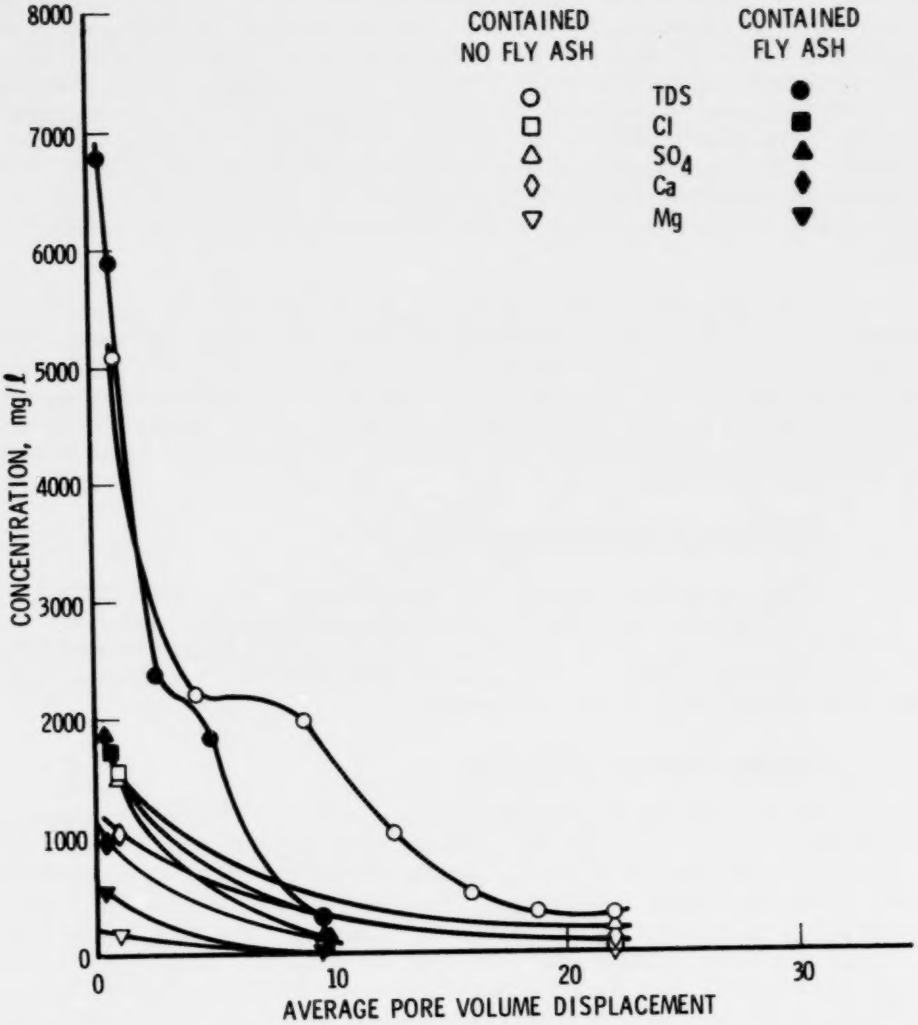


Figure 29. Concentration of major species in leachate of second-stage slurry solids of RTP oxidized sludges

TABLE 28. PHYSICAL CHARACTERISTICS OF RTP OXIDIZED SLUDGES

Sample Designation	Moisture Content, %	Density, g/cm^3 (wet)	Unconfined Compressive Strength, kg/cm^2		Density, g/cm^3 (dry)	Pore Volume Fraction	Permeability Coefficient, cm/sec[1]
			(wet)	(dry)[b]			
Sampled 9/30/75, Contained Fly Ash							
First-Stage Slurry[c]	10	1.4	4.4	0.7	1.3	0.50	1.6×10^{-4}
Second-Stage Slurry[d]	14	1.2	1.1	0.5	1.0	0.60	8.1×10^{-5}
Filtered Solids[e]	18	1.5	1.4	0.9	1.2	0.50	4.5×10^{-5}[a]
Sampled 12/4/75, Contained No Fly Ash							
First-Stage Slurry	15	1.3	4.2	3.0	1.1	0.55	1.1×10^{-4}
Second-Stage Slurry	14	1.0	---	1.9	0.8	0.65	9.6×10^{-5}
Filtered Solids	18	1.35	1.8	1.6	1.1	0.55	1.1×10^{-4}

[a] Test specimen was prepared by "rodding" slurry during initial drainage.

[b] 50°C, vacuum.

[c] Gypsum sludge.

[d] Sulfite sludge.

[e] Gypsum sludge with 5 percent sulfite "impurity."

corresponding dimensional measurements, the wet and dry densities shown in Table 28 were determined. Densities of the dried samples were generally about 20 percent lower than the densities measured before drying. Pore volume fractions computed from the dry densities ranged from 0.50 to 0.65, of which from 30 to 50 percent remained filled with moisture when the cast samples were allowed to drain and dry in the ambient air until firm enough for compressive strength measurements. Both, for samples with and for those without fly ash, the second-stage solids showed the largest pore volume fractions and the lowest densities, but the filtered solids retained the largest percentage of water. The pore volume fractions of the samples that contained no fly ash were slightly higher and their densities slightly lower than for the corresponding samples that had no fly ash.

8.3.3 Unconfined Compressive Strength

The unconfined compressive strengths of wet and dry samples are shown in Table 28. A comparison of the results for the two sets of samples shows that when wet, the corresponding members of both sets had comparable strengths, but when totally dry the samples that contained no fly ash had higher compressive strengths. Furthermore, for both sets of samples the first-stage solids when wet showed substantially higher compressive strengths than did the second-stage slurry solids or filtered solids.

The analyses of the filtered solids samples showed approximately 5 percent calcium sulfite hemihydrate (Table 26) with the first-stage solids containing only negligible amounts. It is believed that the presence of this hemihydrate in the filtered solids is responsible for the greater retention of water and for the lower compressive strengths relative to the first-stage solids.

8.3.4 Load-Bearing Strength

Load-bearing strengths were measured on both samples of filtered solids, with and without fly ash, using an adaptation of the standard bearing ratio test for soils, ASTM D-1833-73 (Ref. 11). These gypsum samples, which contained 5 percent sulfite, exhibited strength characteristics of sludge containing typically sulfite-sulfate ratios of 3 to 4.

Measurements were repeated after further dewatering of the solids. Results for the filtered solids with and without fly ash are plotted in Figure 30. Although the measurements were terminated prematurely for the sample containing fly ash, the curves are similar for the two samples except that the rapid increase in strength with increasing solids content occurs at about 10 percent higher solids content for the sample containing fly ash.

8.4 COST ESTIMATES OF GYPSUM-PRODUCING PROCESSES

Engineering cost estimates were made for producing wallboard grade gypsum from forced oxidation of limestone-scrubbed flue gas desulfurization (FGD) sulfite-rich wastes. Two basic processes were considered:

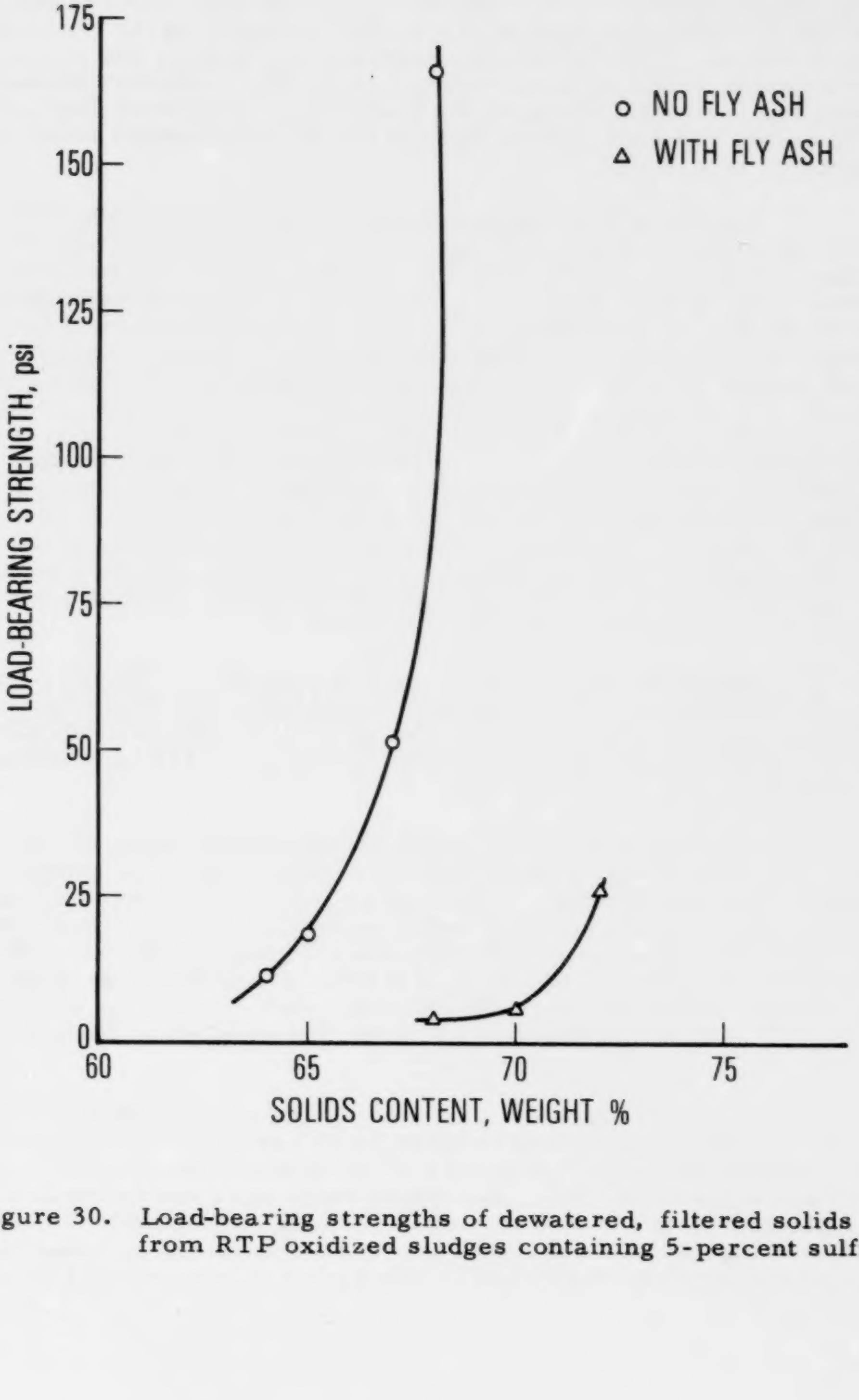


Figure 30. Load-bearing strengths of dewatered, filtered solids from RTP oxidized sludges containing 5-percent sulfite

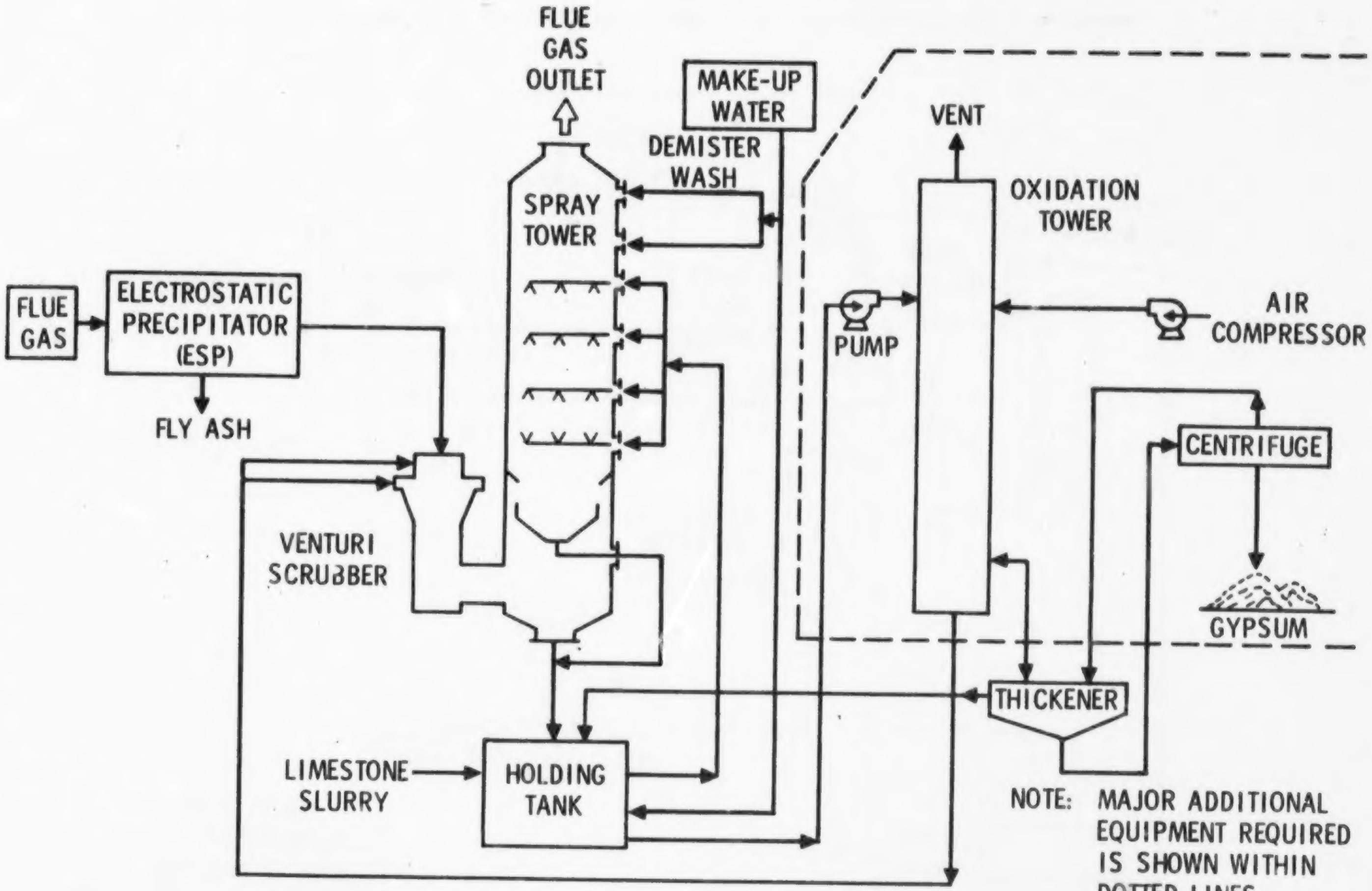
a tail-end system incorporating an oxidation tower and an integrated system which represents the pilot plant illustration of Borgwardt at RTP, which was tested at the TVA Shawnee Plant with a 10-MWe venturi-spray tower scrubber (Figures 31 and 32). The estimates are meant to illustrate the range of costs for saleable-grade gypsum produced from SO_2 abatement processes. The economics were also evaluated for converting sulfite-rich flue gas cleaning (FGC) wastes to a high gypsum content for environmentally sound disposal aboveground or in a landfill.

Results of the calculations indicated that for a 500-MWe tail end forced oxidation system, total capital costs are approximately 20 percent greater than for a base case system that includes particulate removal by an electrostatic precipitator (ESP) and a limestone scrubber system producing sulfite-rich sludge. A schematic of the basic particulate removal and scrubber system considered as a baseline and the major additional equipment to oxidize the sulfite-rich slurry are depicted in Figure 31. It illustrates a two-stage (venturi-spray tower) limestone wet-scrubber system with a tail-end oxidation tower incorporated to oxidize the sulfite-rich slurry to gypsum. In order to account for the production of saleable material with a sufficiently low moisture content, centrifugation was included. Capital equipment costs for the integrated system (Figure 33) were estimated to be about 13 percent more than the base case scrubber. This configuration is approximated by the pilot plant system tested by Borgwardt of EPA (Ref. 14), which is currently being evaluated at the TVA Shawnee Power Plant, Paducah, Kentucky, by EPA, TVA, and Bechtel at the 10-MWe level.

The base case scrubber capital costs for a 500-MWe scrubber system, in 1977 dollars, were estimated at $94/kW. The figure excludes disposal costs and was the average of five units in the 450- to 550-MW range reported in Reference 15 and corrected to 1977 costs based on methods used in Reference 3.

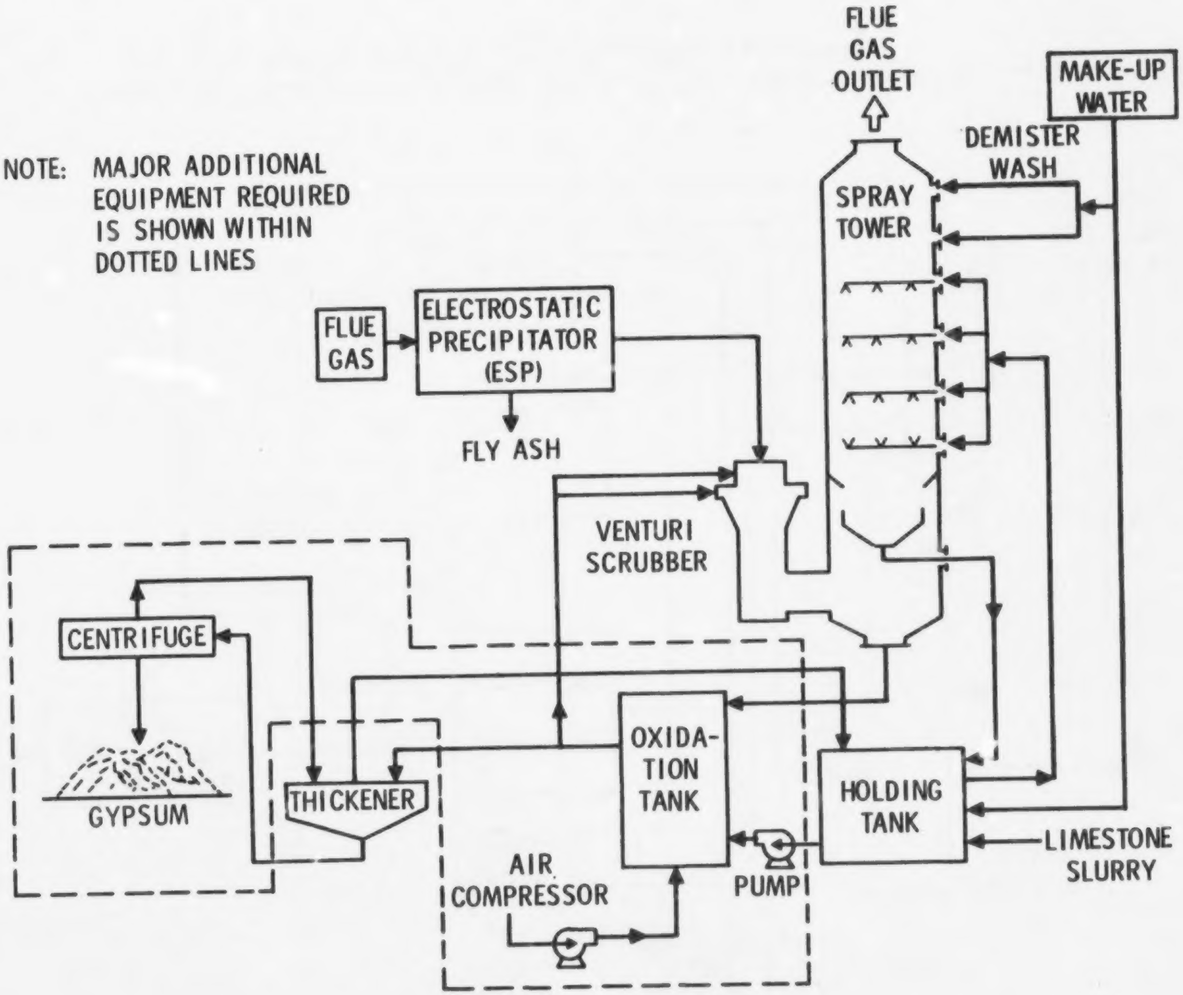
The major pieces of additional equipment required for oxidizing the sludge with the tail-end system includes oxidation towers, pumps, air compressors, and centrifuges. Individual equipment costs were taken from Reference 16 and corrected to 1977 based on factors obtained from Reference 17. The total increase in costs for these items, for the tail-end system which is shown in Table 29, was $\$10.14 \times 10^6$. A significant savings in equipment costs can be realized with the integrated system; the corresponding increase in capital equipment costs above the baseline is $\$6.64 \times 10^6$, (Table 29).

Annual charges for the oxidation-related equipment based on a 30-year life for the equipment were taken as 18 percent of the capital costs (Ref. 3). Annual operating costs of $\$2.87 \times 10^6$ were based on data from Reference 18 and adjusted to 1977. Limestone costs were estimated at $6/ton, and for a plant operating load factor of 50 percent, totalled $\$0.75 \times 10^6$/year. The base case capital and operating costs are summarized in Table 30. Gypsum-production costs discussed in subsequent paragraphs are assumed


FLUE GAS
ELECTROSTATIC PRECIPITATOR (ESP)
FLY ASH
FLUE GAS OUTLET
SPRAY TOWER
MAKE-UP WATER
DEMISTER WASH
VENTURI SCRUBBER
LIMESTONE SLURRY
HOLDING TANK
VENT
OXIDATION TOWER
PUMP
AIR COMPRESSOR
CENTRIFUGE
GYPSUM
THICKENER

NOTE: MAJOR ADDITIONAL EQUIPMENT REQUIRED IS SHOWN WITHIN DOTTED LINES

Figure 31. Simplified process schematic for wet-limestone tail-end scrubber forced-oxidation gypsum-producing system


FLUE GAS OUTLET
MAKE-UP WATER
DEMISTER WASH
SPRAY TOWER
FLUE GAS
ELECTROSTATIC PRECIPITATOR (ESP)
FLY ASH
VENTURI SCRUBBER
CENTRIFUGE
GYPSUM
THICKENER
OXIDA-TION TANK
HOLDING TANK
LIMESTONE SLURRY
AIR COMPRESSOR
PUMP

NOTE: MAJOR ADDITIONAL EQUIPMENT REQUIRED IS SHOWN WITHIN DOTTED LINES

Figure 32. Simplified process schematic for wet-limestone integrated forced-oxidation gypsum-producing system

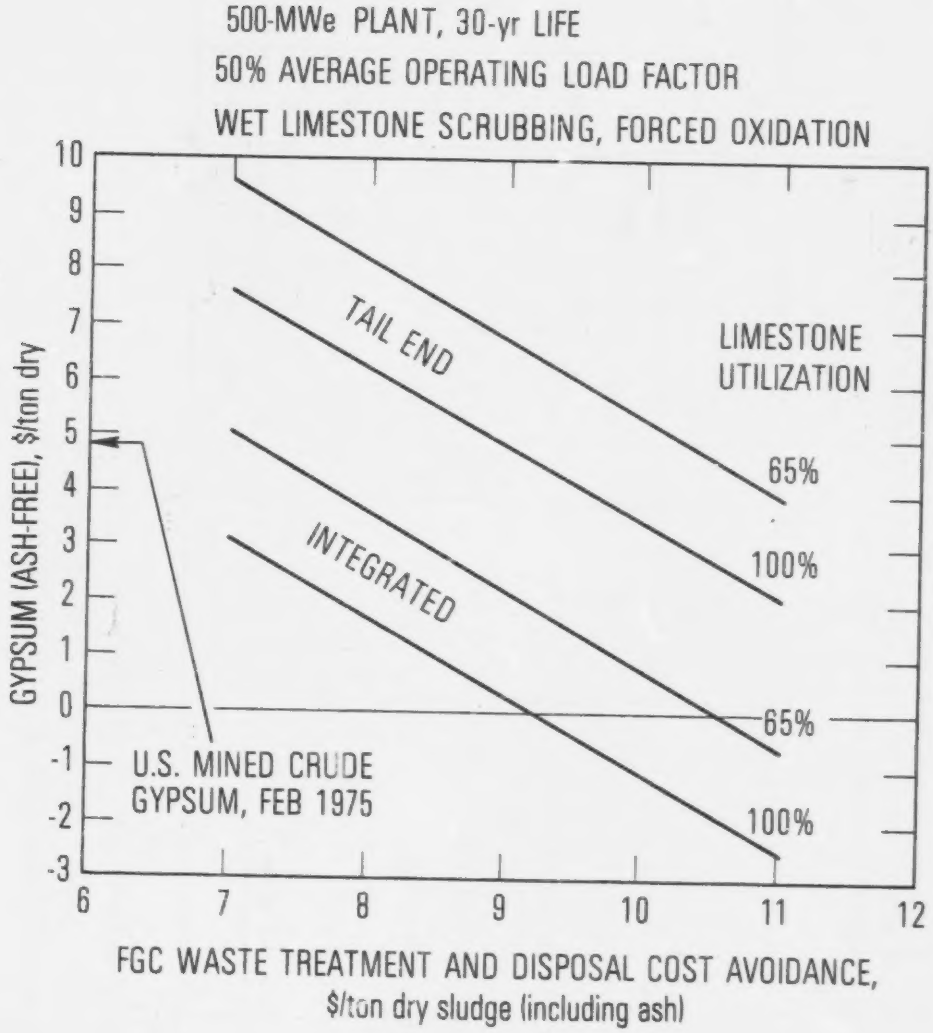


Figure 33. Cost of producing saleable gypsum as a function of sludge treatment and disposal credit, 1977 dollars

TABLE 29. COST OF MAJOR COMPONENTS OF FORCED OXIDATION, WET LIMESTONE SCRUBBING SYSTEM FOR A 500-MWe PLANT, 1977 DOLLARS[a, b]

Equipment	Equipment Life, yr	Tail-End System Total Cost	Integrated System Total Cost	Ref.
Oxidation Towers (15 × 50 ft, 2 each)	15	\$ 4.20×10^6	Not req'd	16
Air Compressors (30% spare capacity)[c]	15	3.75×10^6	3.75×10^6	16
Pumps (50% spare capacity)[c]	10	0.52×10^6	0.52×10^6	16
Scroll-type Centrifuge (25% spare capacity)[c]	15	0.75×10^6	0.75×10^6	16
Piping (estimate, 10%)		0.92×10^6	0.92×10^6	
Oxidation Tank (20,000 gal, 2 each)	15	Not req'd	0.70×10^6	16
Total		\$ 10.14×10^6	6.64×10^6	

[a] 30-year plant life; estimate includes installation.

[b] Dry gypsum produced: 1.37×10^5 tons/yr; slurry pumped: 500 gpm.

[c] Spare capacity based on a minimum of 7000 hr/yr operation.

TABLE 30. BASE CASE COSTS FOR WET LIMESTONE SCRUBBING SYSTEM FOR A NEW 500-MWe PLANT IN 1977 DOLLARS[a]

	Total	Annual	Ref.
Capital Costs at \$94/kW	$\$47.00 \times 10^6$		15
Annual Charges at 18%	--	$\$\ 8.46 \times 10^6$	3
Operating Costs	--	$\$\ 2.87 \times 10^6$	18[c]
Limestone at \$6/ton	--	$\$\ 0.75 \times 10^6$	18
Total[b]		$\$12.08 \times 10^6$[c]	
\$/Ton Coal		\$12.57	
Mills/kWh		\$ 5.53	

[a] 30 year life; 50% average operating load factor (4380 hr/yr); tons coal burned, 9.6×10^5 tons/yr (3.5% S, 12% ash, 0.88 lb/kWh; kWh generated, 2.18×10^9/yr; dry sludge, 1.93×10^5 tons/yr (includes 0.87×10^5 tons/yr fly ash); 90% SO_2 removal; 0.65 limestone utilization factor; limestone consumption, 1.25×10^5 tons/yr.

[b] Escalated at 6% annually from 1973 estimate for 500-MWe plant.

[c] Does not include FGC waste disposal costs.

to be independent of the base case capital and annual operating costs, inasmuch as gypsum modifications are estimated and presented on an incremental basis. On this basis, the effect of forced oxidation can be compared directly to the waste disposal costs by chemical treatment and landfill or by a number of other disposal options.

The estimate of $\$10.14 \times 10^6$ results in a cost of \$17.51 and \$15.62 per ton of dry gypsum for a limestone utilization factor of 0.65 and of 1.0, respectively (Table 31). It does not consider the cost of disposing of the waste which would be incurred if the sludge were not oxidized. Based on a midrange value of \$9.00/ton, dry, for FGD sludge chemical treatment and disposal (Ref. 3), which would offset the gypsum processing costs, and assuming a \$3.00/ton fly ash disposal cost, the net cost of producing gypsum in a tail-end system is \$6.73 and \$4.84/ton dry gypsum for the 0.65 and 1.0 limestone utilization factors, respectively (Table 32). The effect of improved limestone utilization is highly significant in reducing the net gypsum cost. A larger effect in reducing the production cost is realized by using an integrated system. With the economies resulting with that mode of operation, the estimates are \$2.22 and \$0.31 per dry ton, respectively, for utilization of 65 and 100 percent. Tests have shown (Ref. 19) that a utilization of virtually 100 percent can be achieved with the process and that goal should be considered in the oxidation process. The 65 percent factor is provided for both methods to place the costs in perspective. To be more realistic, the gypsum may contain as much as 8 percent moisture and therefore would cost approximately 8 percent less per ton of moist gypsum.

Operating tests have also indicated that the settling properties of gypsum are significantly superior to those of calcium sulfite. Therefore, smaller thickeners can be used, which reduces plant capital costs. This refinement has not been included in the estimate. In addition, better, trouble-free scrubber operation has been reported with a forced oxidation system, providing further potential areas for reducing the operating cost attributable to forced oxidation.

A comparison of mined gypsum cost with forced oxidation saleable gypsum costs that include credit for sludge disposal is shown in Figure 33. For the tail end oxidation systems and 100 percent limestone utilization, a \$9/ton chemical treatment and disposal avoidance cost results in a gypsum cost comparable to the 1975 fob price of \$4.80/ton for domestic gypsum (Figure 33). At lower disposal costs, forced oxidation economics of tail-end systems are not as favorable, and at greater than \$9/ton they become increasingly attractive. Over the entire range of sludge disposal cost avoidance of \$7 to \$11/dry ton of sludge, gypsum from the integrated system is competitive with the mined gypsum.

An assessment was made of these costs to determine gypsum disposal costs which when added to the cost of forced oxidation would equal the cost for disposal of a comparable quantity of sulfite sludge. The results are plotted in Figure 34 which portrays the values for tail-end and integrated

TABLE 31. TOTAL INCREMENTAL COST OF GYPSUM-PRODUCING SYSTEM FOR A 500-MWe PLANT IN 1977 DOLLARS[a] (AS COMPARED TO SCRUBBING)

Forced Oxidation Cost Increment	Total		Annual			
			Tail End		Integrated	
			Utilization Factor			
	Tail End	Integrated	0.65	1.0	0.65	1.0
Capital Cost	10.14×10^6	6.64×10^6	--	--	--	--
Annual Charge at 18%	--	--	1.82×10^6	1.82×10^6	1.20×10^6	1.20×10^6
Annual Labor[b]	--	--	0.58×10^6	0.58×10^6	0.58×10^6	0.58×10^6
Limestone[c]	--	--	d	(0.26×10^6)	d	(0.26×10^6)
Total			2.40×10^6	2.14×10^6	1.78×10^6	1.52×10^6
$/Ton Coal			2.50	2.22	1.85	1.58
Mills/kWh			1.09	0.98	0.82	0.70
$/Ton Dry Gypsum			17.51	15.62	13.00	11.09

[a] Relative to wet limestone scrubbing without waste disposal, 30-year life plant, 50% average load factor.

[b] Prorated on the basis of scrubber system operation.

[c] Limestone used at 1.0 utilization factor = 0.81×10^5 tons/yr.

[d] Included in scrubber costs.

TABLE 32. ESTIMATED INCREMENTAL COST OF PRODUCING GYPSUM FOR SALE OR DISPOSAL RELATIVE TO THE DISPOSAL OF CHEMICALLY TREATED FGC WASTE, IN 1977 DOLLARS[a]

Item	Saleable (Ash-Free)				Disposable (Including Ash)	
	Tail End		Integrated		Tail End	Integrated
Limestone Utilization Factor	0.65	1.0	0.65	1.0	1.0	1.0
Gypsum[b]	$17.51	$15.62	$13.00	$11.09	$ 9.55	$ 6.79
Ash Disposal[c]	1.90	1.90	1.90	1.90	N/A	N/A
Sludge Treatment and Disposal Cost Avoidance at $9.00/Dry Ton Sludge with Ash	(12.68)	(12.68)	(12.68)	(12.68)	(12.68)	(12.68)
Cost Avoidance, Filtering	N/A	N/A	N/A	N/A	(0.55)	(0.55)
Total Incremental Cost of Gypsum/Ton (Dry):	$ 6.73	$ 4.84	$ 2.22	$ 0.31	$ (3.68)	$ (6.44)
$/Ton Coal	0.96	0.68	0.32	0.04	(0.52)	(0.90)
Mills/kWh	0.42	0.30	0.14	0.02	(0.23)	(0.40)

[a] All costs are converted to $/ton dry gypsum except as noted; 500 MWe plant, 30-yr life, 50% average load factor, wet limestone scrubbing, forced oxidation.

[b] Gypsum-sulfite sludge quantities, dry ton/yr:

	Dry Ton/Year	
	Ash-Free	With Ash
Gypsum	1.37×10^5	2.24×10^5
Sulfite Sludge	1.06×10^5	1.93×10^5

[c] Estimated at $3/ton dry ash and converted to $/ton dry gypsum.

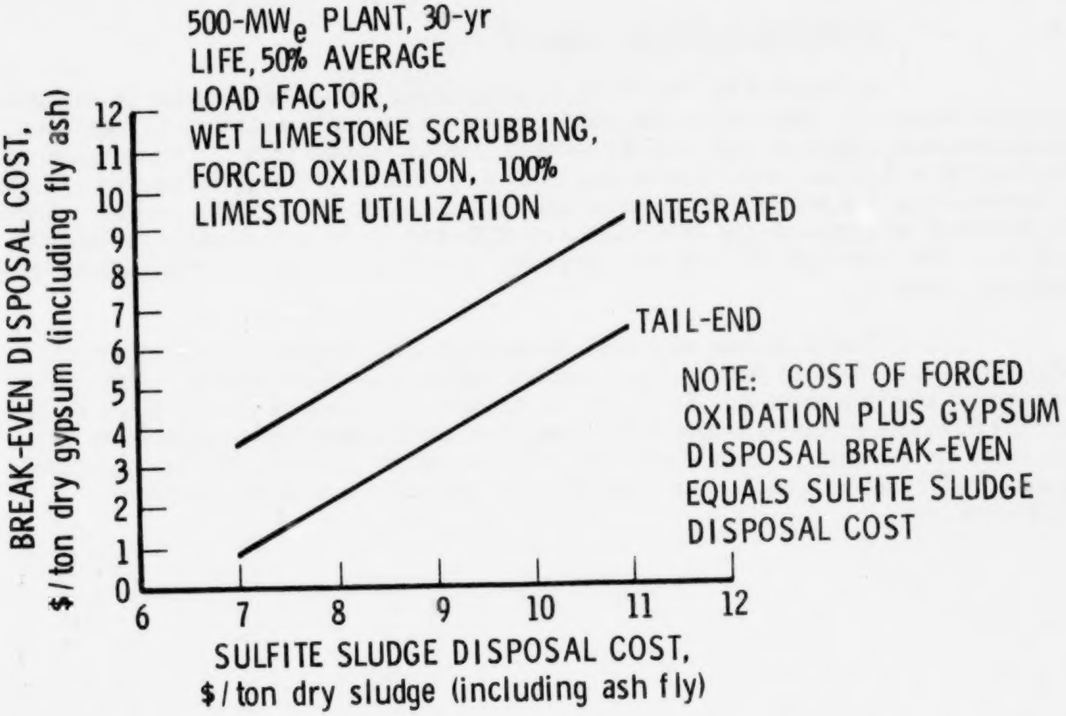


Figure 34. Gypsum disposal cost allowable to limit forced oxidation to cost of disposal of comparable quantity of sulfite sludge, 1977 dollars

oxidation systems. Data consistent with the approach shown in Table 32 were used to determine Figure 34. In that figure, it can be seen, for example, that if sulfite sludge disposal costs $9/ton of sludge (dry, including ash), the break-even cost for disposal of gypsum (dry, including ash) from an integrated system would be approximately $6/ton. From the standpoint of disposal only, any cost of disposal for gypsum in excess of $6/ton would make forced oxidation more expensive than sulfite production and disposal. For a tail-end system, the gypsum disposal break-even cost would be about $3.50 if sulfite-rich sludge disposal is $9.00 (Figure 34). These comparisons can be repeated for any sludge disposal cost between $6 and $12/ton of sludge, using Figure 34.

8.5 GYPSUM COST SUMMARY

In summary, the cost of producing saleable gypsum in integrated systems results in generally favorable economic trends relative to chemical treatment and disposal costs of $7 to $11/ton of sludge (dry). Significant to this fact is a $2/ton reduction in the cost of producing the gypsum, which can be achieved by improving limestone utilization from 65 to 100 percent. Landfill disposal of gypsum-fly ash mixtures appears to be marginally competitive with disposal costs at $8/dry ton; gypsum economics improve with increasing disposal costs.

For tail-end systems operating with 100 percent limestone utilization, the cost of producing saleable gypsum is marginally competitive if disposal costs are in the $8 to $9/ton range. Limestone utilization of less than 90 percent tends to make this method of utilization noncompetitive with chemical treatment. The economics of disposal of gypsum-fly ash mixtures from a tail-end system do not appear to be competitive with chemical treatment.

SECTION IX

EVALUATION OF THE ENVIRONMENTAL ACCEPTABILITY OF FGD SLUDGE

9.1 INTRODUCTION

The data presented in this study pertain to the phenomenological behavior of flue gas desulfurization (FGD) sludges that is expected in field disposal. The behavior has been separated into chemical and physical properties, and experiments have been conducted in a manner so as to simulate as closely as practicable the environmental conditions expected in actual field disposal. Thus, the range of experiments has included the disposal conditions considered pertinent from environmental and economic points of view.

This section of the report discusses the expected impact of FGD sludges on the environment with respect to the range of properties observed in this study. It is presumed in these discussions that the range of properties observed in the sludge samples are representative of the sludges that are being and will be produced. In the sampling of this study, an attempt was made to provide representation for Eastern and Western coals, lime, limestone, and double alkali systems; sludges with and without fly ash; and systems operating at both high and low pH. Although not every combination of variables could be included, it is believed that the following discussions will be valid for a majority of the sludges that require disposal.

In order to evaluate the environmental acceptability of alternative disposal techniques for FGD wastes, it is necessary to assess the various routes by which chemical pollutants may enter the environment from a disposal site and to determine the relative mobility of the various chemical species with respect to their environmental accessibility. Thus, in addition to chemically characterizing FGD sludges, this task effort includes experimental determination of the potential pollution impact that is inherent in each of the various disposal techniques. The assessment of the potential pollution impacts includes considerations of the chemical state of the pollutant and the route by which it may enter the environment.

9.2 BACKGROUND

In previous reports (Refs. 1 and 2), the various potential routes of chemical pollution from disposal sites and some of the alternative methods by which FGD may be disposed were discussed. The following subsections review the highlights from these reports and provide an assessment of their technical and economic viability for FGD waste disposal.

9.2.1 Alternative Routes of Pollution

Several potential routes of environmental pollution have been identified, but generally they are reduced to either pollution of air or pollution of water. Experimental investigation showed that pollution of air by vapor species, either volatilization or dissociation of sulfite or sulfate, cannot occur even in extreme climatic conditions. A form of airborne pollution can exist by wind-whipped spray from the surface of a disposal pond, but this form of pollution is generally localized and limited in effect.

Pollution of water is by far a more likely source of potential environmental pollution either from surface runoff or from leaching of the disposal basin with rainwater. The assessment of data on runoff suggests that a siltation pond be used during placement of treated FGD waste and that overburden be used to prevent runoff pollution from erosion attack by rain, freeze-thaw, or wet-dry cycles.

The most serious form of pollution potential exists as a consequence of the action of rainwater leaching through a disposal basin. Leaching data from laboratory experiments show that the concentration of major species in the leachate is rapidly reduced in both chemically treated and untreated sludges, but the absolute concentration of the treated material is about one-half that of untreated material initially, after which they tend to converge. A steady-state concentration of total dissolved solids (TDS) in the leachate is maintained after about five pore volumes displacement (PVD) at 2000 to 2200 mg/ℓ and primarily is representative of the equilibrium dissolutions of gypsum. Trace elements generally were reduced to values below detection limits during the initial pore flushing of the column, and no appreciable effect of chemical treatment could be discovered. Only lead, selenium, and zinc were ever found in detectable quantities after steady state was established. The leachate quality of columns controlled in aerobic conditions differed in a predictable manner from an anaerobic leachate, but neither created a leachate markedly different from the other.

The primary advantage of chemical treatment is the conversion of the sludge to a load-bearing material and a reduction of the coefficient of permeability by at least one order of magnitude. When placed in a landfill it can be contoured to prevent the collection of rainwater so that the potential for seepage is eliminated or greatly minimized. If the placement of the material is such that rainwater and sludge liquor are collected on its surface or if some seepage occurs during a runoff condition, the reduction of both the permeability and concentration of major species reduces the mass release of sludge constituents to the subsoil when compared to untreated sludges.

9.2.2 Alternative Disposal Techniques

9.2.2.1 Ponding

The method that represents the least deviation from state-of-the-art fly ash disposal is direct ponding into a disposal basin. The environmental impact of pond disposal is strongly dependent upon the ability (1) to contain the components of a sludge so as to prevent environmental pollution and (2) to retire the disposal site in a manner that does not create a safety hazard or nuisance in subsequent land use. For pond disposal, the environment can be protected from chemical pollution principally from leachate contamination of groundwater, by lining the pond basin with clay, impermeable soil cements, or synthetic sheeting material. Also, some natural clay deposits have sufficiently low permeabilities that sludge disposal can be safely contained in a natural basin.

While chemical pollution may be avoided through proper pond management, ultimate pond retirement may not be effected in an environmentally sound manner. Although a pond may be evaporated and possibly air-dried and covered with overburden, an acceptable procedure of this sort has not been demonstrated. Moreover, the question of land reuse or eventual pollution by a breach in a pond liner cannot now be answered.

9.2.2.2 Chemical Treatment

The method by which FGD sludge is treated chemically to increase its structural stability and to reduce leachable chemical components or reduce its permeability is offered by several commercial processors. Chemically treated sludges can be used as landfill in both submerged and above-grade conditions. For any chosen disposal condition, chemical treatment provides improvements in the environmental acceptability of FGD wastes. While the environmental acceptability of treated sludges appears to be favorable under most disposal methods, the added environmental assurance afforded by the chemical process increases the cost of disposal.

9.2.2.3 Other Methods

An alternative method of sludge disposal is one which oxidizes sulfite sludges to form gypsum, which can then be dewatered to a high solids content (greater than 75 percent). This material is easy to handle after dewatering and when stored or disposed of above ground, it tends to shed water, generally, with a minimum amount of erosion of the gypsum. Control of runoff may be required. An evaluation of this method is being conducted at the U.S. Environmental Protection Agency/Tennessee Valley Authority (EPA/TVA) Shawnee Test Site in Paducah, Kentucky (Ref. 4).

Another alternative method of FGD waste disposal is by pond underdrainage. This method requires a closed basin in which the waste at any water content may be placed, and excess water is returned to the scrubbing system from an underdrainage system. A detailed description of this method is presented in the following section and describes the work in this report period. A field evaluation of this process is discussed in Ref. 4.

Also, ocean and mine disposal are being investigated in other EPA studies, References 5 and 6. Under appropriate conditions, it appears that these methods can be practical.

9.3 THE UNDERDRAINAGE METHOD FOR DEWATERING FGD SLUDGE

A simple, economical, and widely applicable method may exist for changing a scrubber sludge impoundment from what would otherwise be a structural and environmental liability to a condition acceptable for landfill and other ultimate uses. The method requires that, prior to introduction of the sludge, the location for the impoundment be provided with underdrainage facilities for removal of the sludge seepage and rainfall as it collects subsequently and drains. Because no accumulation of either liquor or leachate is provided to a hydraulic head, no soluble sludge constituents are carried into the soil and ultimately to the underground water table. Therefore, pond liners or impervious clay are not necessary prerequisites of a sludge impoundment except in rare cases of high soil permeability or high water tables. When the impoundment is filled, it can be retired, equipped with a covering of soil, and the land can then be reclaimed for other uses. So far as it is now known, this method is applicable to all the sludges now being produced by current scrubbing processes. This method is now being evaluated at TVA Shawnee as part of the EPA-sponsored sludge disposal field evaluation project. Two ponds provided with facilities for underdrainage have been filled, one with lime process sludge and the other with limestone process sludge. These two ponds are now being monitored, along with five others previously filled with either untreated or chemically fixed sludge. The data presented herein represent the results of limited laboratory tests conducted immediately prior to the filling of the ponds at Shawnee. The purpose of the tests was to identify optimum compositions and conditions for producing a structurally suitable ponded material. Tests were not designed to study the effects of all parameters, and not all of those parameters which were investigated were systematically varied so as to obtain the most definitive conclusions.

9.3.1 Results

The load-bearing strength curves of Figure 35 show that similar relationships between load-bearing strengths and water content characterize all of the 10 sludge compositions tested. At a certain threshold solids content that is characteristic of each sludge tested, the load-bearing strength increases steeply over a small incremental increase in solids content from a negligible value to well above the minimum for safe access of personnel and equipment. To obtain the data shown in Figure 35, each of 10 sludge samples was dewatered over a period of a few days only by means of underdrainage, and it was shown that each of the sludges tested can be readily dewatered by means of underdrainage to load-bearing strengths that are acceptable for structural purposes.

The lime and limestone ash-free sludges from TVA Shawnee were tested more extensively in the laboratory in support of the field disposal evaluation program (Refs. 3 and 4), and were used to determine the rates of development of load-bearing strength as they were dewatered by underdrainage. Laboratory tests were conducted to determine the loading strengths of the ash-free sludges and of sludge and fly ash mixtures as the samples settled and partially dewatered by means of underdrainage. The fly ash used was obtained from TVA Shawnee and consisted of a mixture of two parts mechanically separated ash and one part electrostatically separated ash. Two samples of filter cake (45 and 48 wt% solids) were obtained from the venturi lime scrubber at Shawnee. The latter sample was obtained during a run in which MgO was added to the scrubber slurry. Centrifuge cake (46 wt% solids) and clarifier underflow slurry (29 wt% solids) were also obtained from the turbulent contact absorber (TCA) limestone scrubber at Shawnee. A second sample of clarifier underflow from the TCA limestone scrubber taken several weeks later was also tested.

In Figure 36, data have been plotted to show the rates of development of compaction strength of wet, ash-free, lime process filter cake and filter cake and fly ash mixtures as they dewater by means of underdrainage. For comparison, Figure 36 also includes plots of the strengths developed by samples containing similar compositions of sludge and fly ash which were allowed to settle without removing any of the water that accumulated at the surface. In the latter case, even after settling for two weeks, the observed strengths were less than 1 kg/cm^2 (14 $lb/in.^2$). In contrast, after one week the underdrained samples had developed strengths ranging from 5 kg/cm^2 (70 $lb/in.^2$) for the sample of ash-free sludge to approximately 20 to 25 kg/cm^2 for the samples of sludge containing 40 percent fly ash. The most rapid development of strength was shown by the sample that had half of the fly ash mixed with the sludge and the other half underlying the sludge and fly ash layer.

Tests were made to determine the effect of compacting the partially dewatered samples. Although repetitive application of compaction loads of 3 psi resulted in increased load-bearing strengths by as much as a

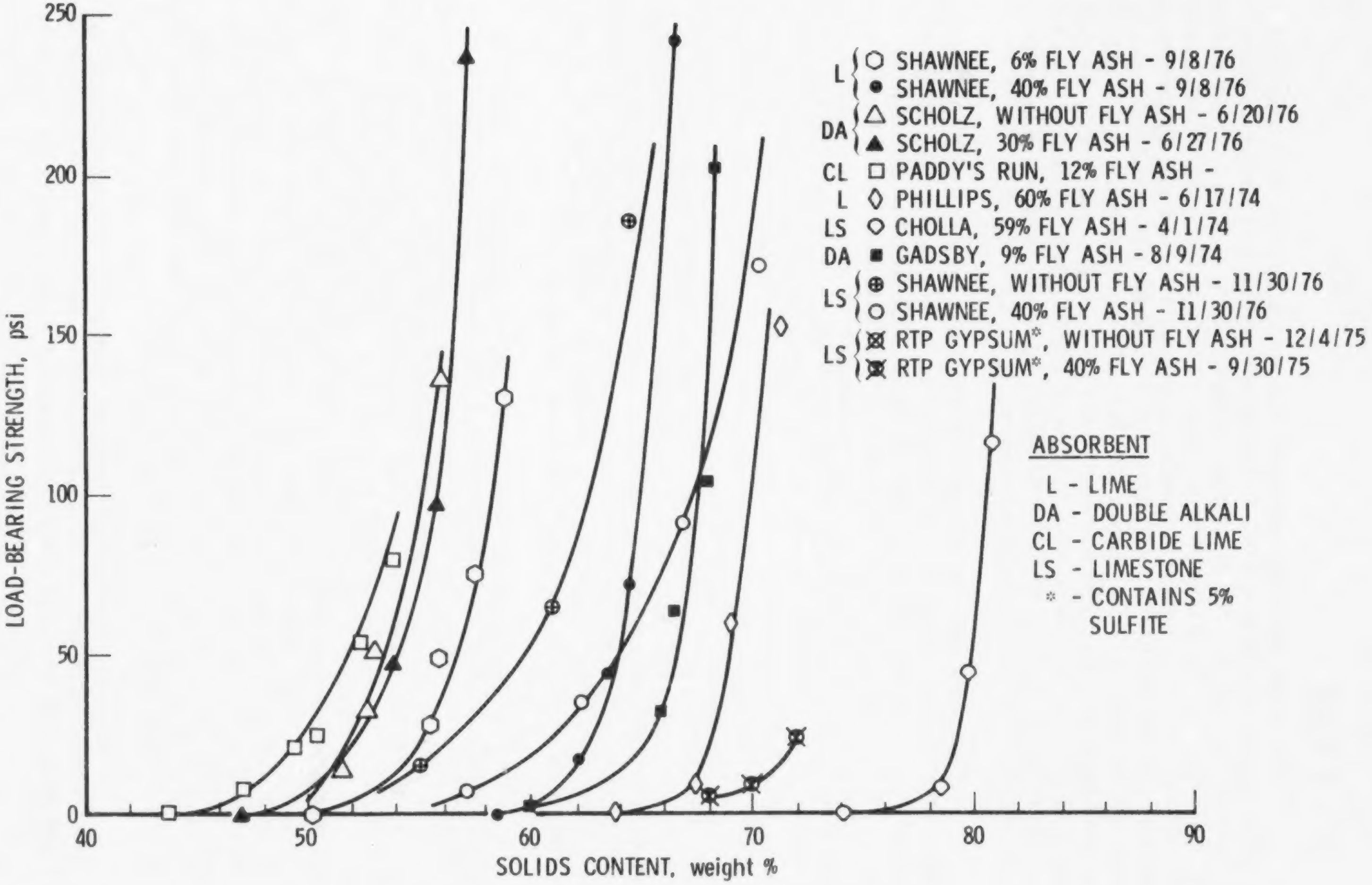
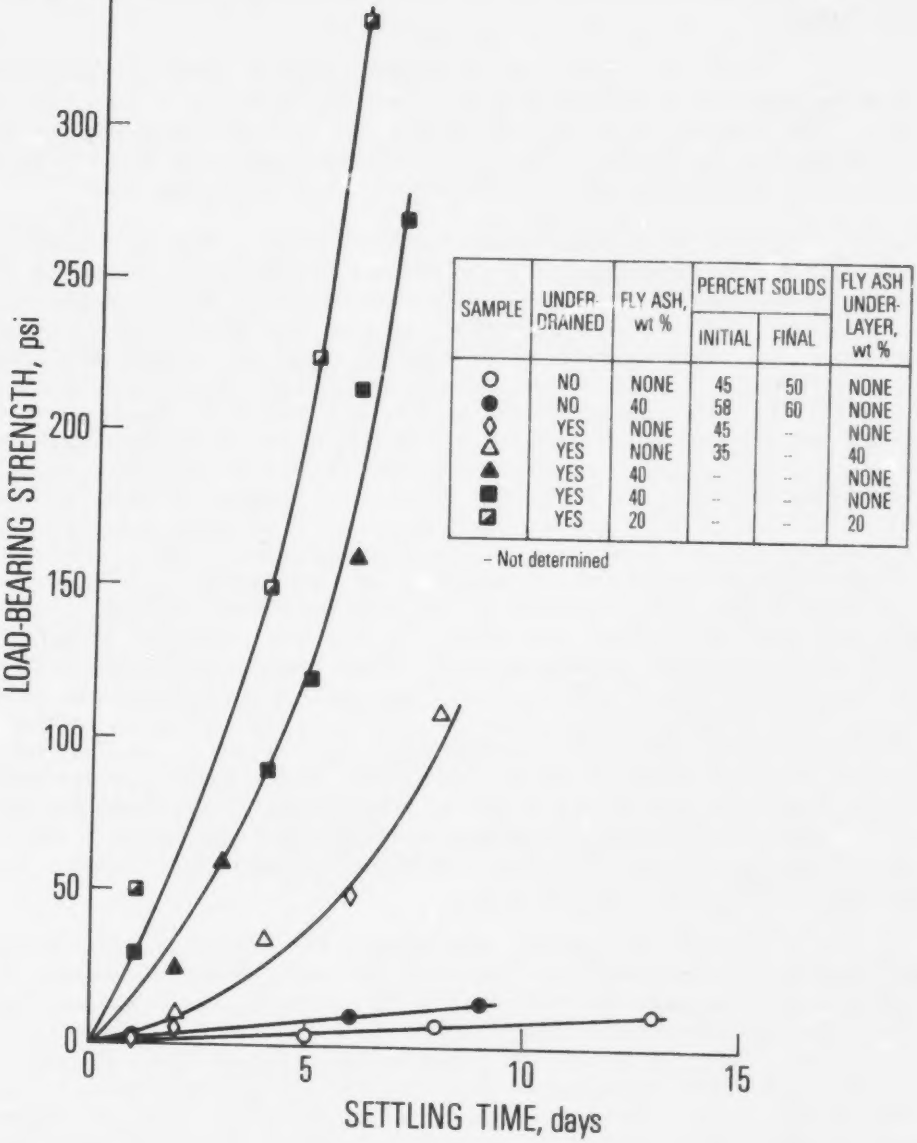


Figure 35. Load-bearing strength as a function of moisture, fly ash content, and sludge origin



SAMPLE	UNDER-DRAINED	FLY ASH, wt %	PERCENT SOLIDS		FLY ASH UNDER-LAYER, wt %
			INITIAL	FINAL	
○	NO	NONE	45	50	NONE
●	NO	40	58	60	NONE
◊	YES	NONE	45	--	NONE
△	YES	NONE	35	--	40
▲	YES	40	--	--	NONE
■	YES	40	--	--	NONE
◪	YES	20	--	--	20

-- Not determined

Figure 36. Development of bearing strength by dewatering of TVA Shawnee lime filter cake and sludge-fly ash mixtures

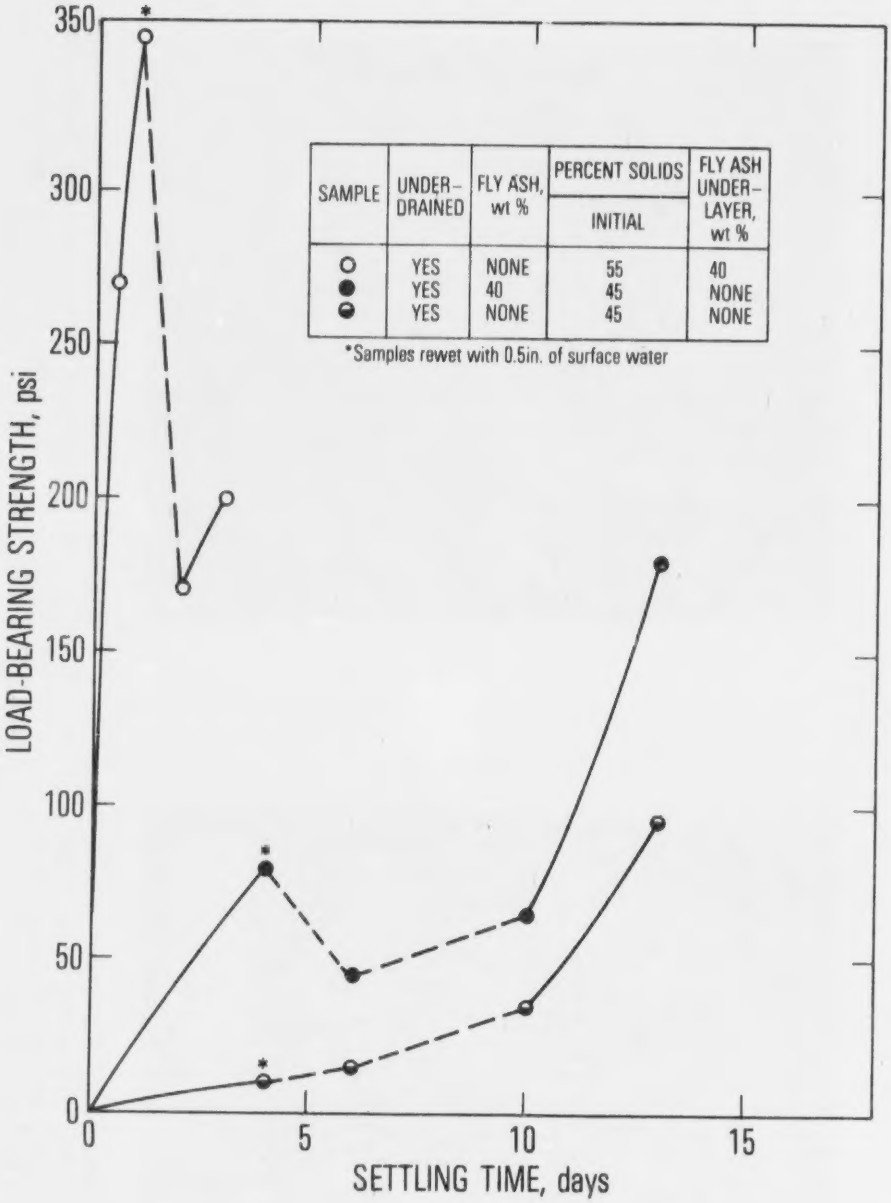
factor of two, this incremental increase was about equivalent to that which would have been obtained by several additional days of dewatering by underdrainage.

Moderate losses in strength resulted from the addition of water to the surface of samples to simulate the effect of a one-half inch rainfall. The results of these rewetting tests are shown in Figure 37. Rewetting caused an initial reduction in strength although the strength was regained after additional time was allowed for dewatering.

Tests were also made with centrifuge cake and clarifier underflow from the limestone TCA scrubber at Shawnee. Samples were prepared by dilution of centrifuge cake with centrate and by removal of supernate from the clarifier underflow to give the 35 wt% solids content in both cases. A second sample of the clarifier underflow was taken two weeks later, which had a 35 wt% solids content and much larger crystals. The solids of this sample settled more rapidly and scanning electron microscope (SEM) photos showed much larger crystals of calcium sulfite hemihydrate, $CaSO_3 \cdot 1/2\ H_2O$, than those of the earlier clarifier underflow sample. For comparison, SEM photos of the three TCA limestone solid samples are shown in Figures 38 through 40. A discussion of crystal morphology is given in Appendix A. Load-bearing strength measurements on these materials as they dewatered by means of underdrainage are shown in the plots of Figure 41. It was observed that the limestone sludge, if left undisturbed, did not dewater as readily as the lime sludge. A skin-like film that formed on the surface sealed off the sample and inhibited further drainage. Puncturing of this surface film caused the samples to resume drainage, with consequent increase in load-bearing strengths as the solids contents increased. Vibration or agitation also accelerated the drainage rates after the formation of the surface film. (This condition has not been evident at any time during two years of monitoring at the field evaluation sites.) Therefore, rates of development of bearing strengths of the limestone sludge and sludge-fly ash mixtures could not be determined with a high degree of reproducibility in the laboratory.

The first clarifier underflow, which was initially 29 percent solids, developed a strength of 5 kg/cm^2 (70 $lb/in.^2$) in one week. When the initial solids content was adjusted to 35 percent, the ash-free clarifier underflow had developed a strength of about 9 kg/cm^2 (128 $lb/in.^2$) at the end of a week. Slightly greater strengths (10 kg/cm^2) were shown by the centrifuge cake. The most rapid gain in strength was shown by the ash-free centrifuge cake with an underlayer of fly ash, which had a loadbearing strength of 18 kg/cm^2 (260 $lb/in.^2$) after six days. Samples with the thicknesses ranging from 4 to 10 in. were tested. All dewatered to comparable strengths although the surfaces of the samples with the greater thickness more readily sealed off and interrupted the drainage.

The solids of the second clarifier underflow sample settled more rapidly, and consequently the rates of development of load-bearing



SAMPLE	UNDER-DRAINED	FLY ASH, wt %	PERCENT SOLIDS	FLY ASH UNDER-LAYER, wt %
			INITIAL	
○	YES	NONE	55	40
●	YES	40	45	NONE
◒	YES	NONE	45	NONE

*Samples rewet with 0.5in. of surface water

Figure 37. Effect of rewetting on development of bearing strength of underdrained TVA Shawnee lime sludge, filter cake, and sludge-fly ash mixtures

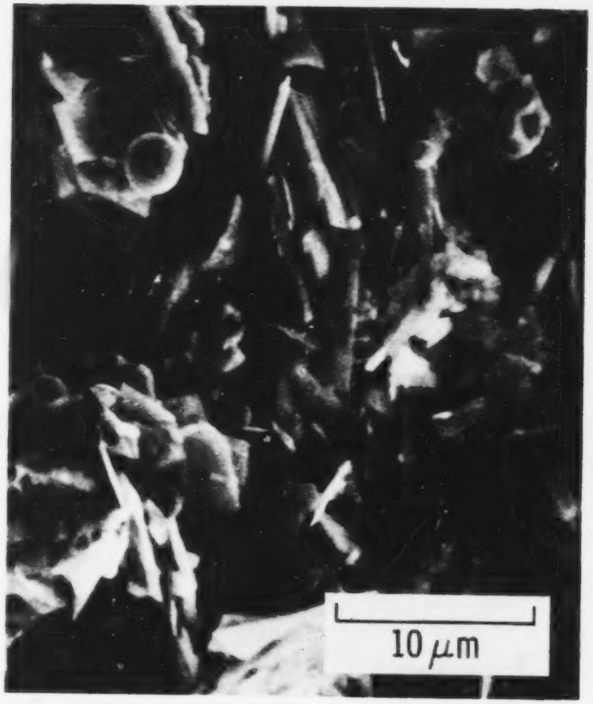


Figure 38. Shawnee TCA limestone sludge solids from centrifuge cake, 45-percent solids (sampled 11/30/76), X3000

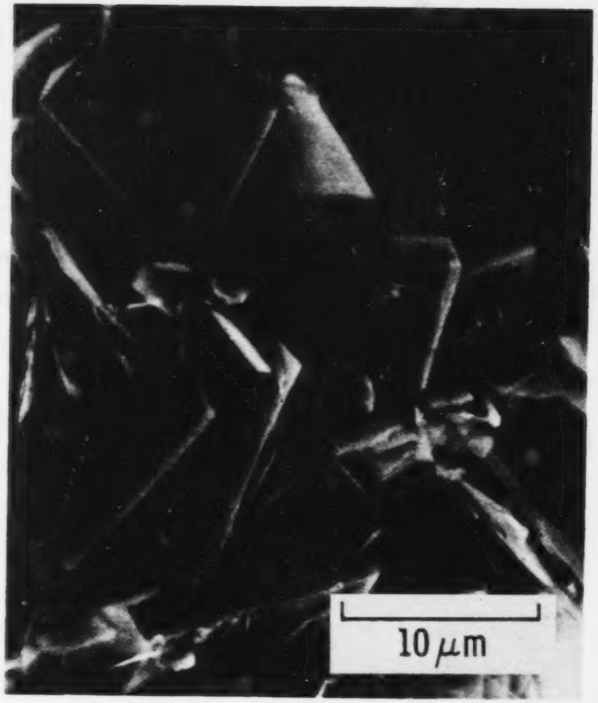


Figure 39. Shawnee TCA limestone sludge solids from clarifier underflow, 29-percent solids (sampled 11/30/76), X3000

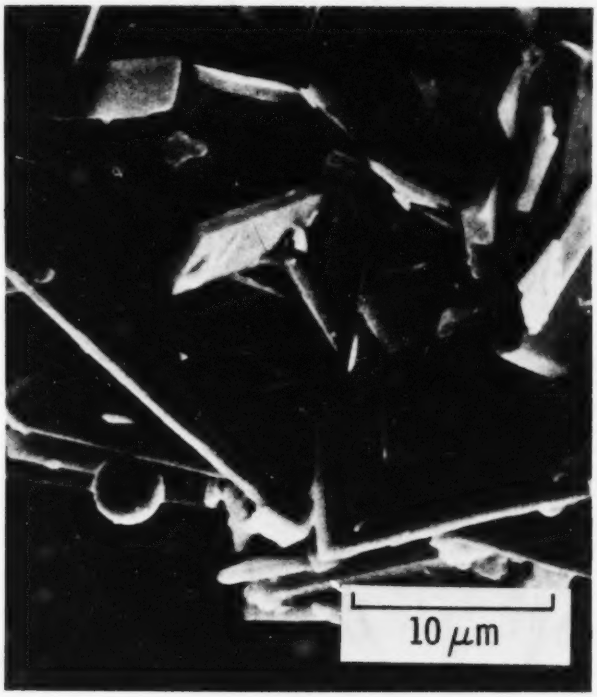
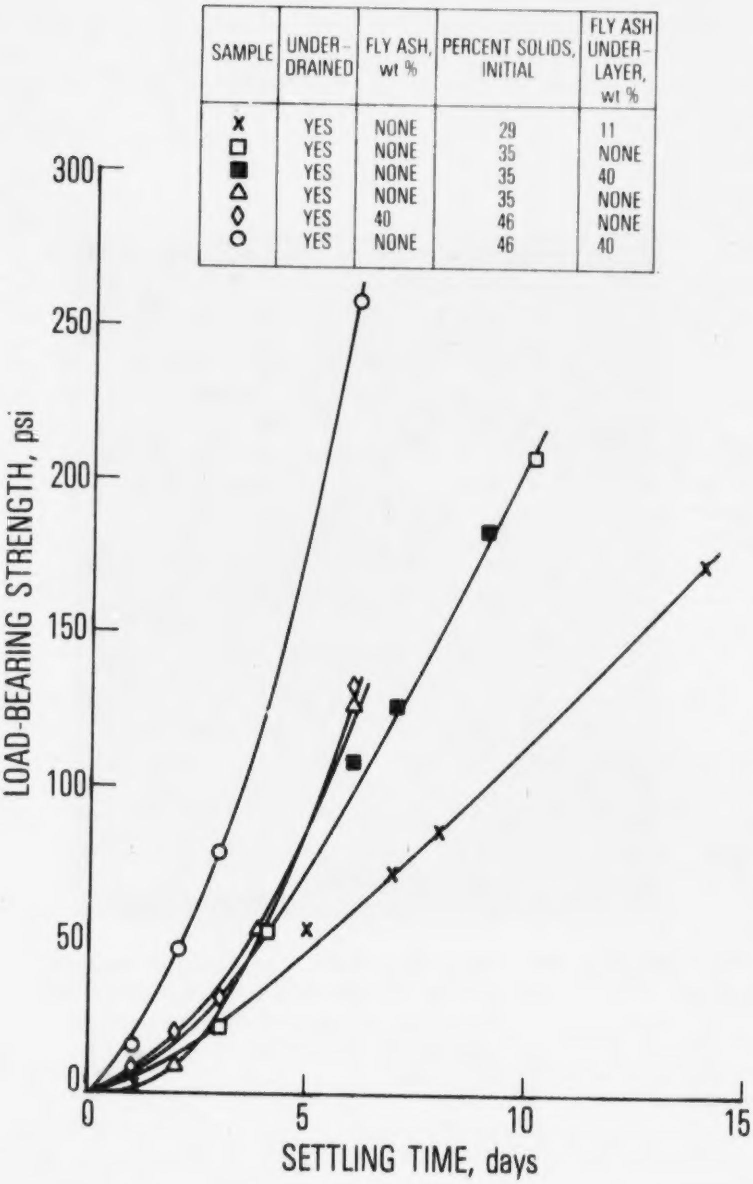


Figure 40. Shawnee TCA limestone sludge solids from clarifier underflow, 35.7-percent solids (sampled 12/1/76), X3000



SAMPLE	UNDER-DRAINED	FLY ASH, wt %	PERCENT SOLIDS, INITIAL	FLY ASH UNDER-LAYER, wt %
x	YES	NONE	29	11
□	YES	NONE	35	NONE
■	YES	NONE	35	40
△	YES	NONE	35	NONE
◊	YES	40	46	NONE
○	YES	NONE	46	40

Figure 41. Bearing strength of underdrained TVA Shawnee limestone sludge and sludge-fly ash mixtures

strengths were accelerated. Although several sludge-fly ash combinations were tested, all developed ultimate strengths in excess of 28 kg/cm^2 (400 lb/in.^{2}), approximately double that of the first sample (Figure 41).

Rewetting of the limestone sludge samples after they had developed significant load-bearing strengths resulted in immediate loss of strength as the surface was partially reslurried. Much of the former strength was regained after subsequent draining, as shown in Figure 42.

In summary, all sludge samples that were provided with a means of dewatering by underdrainage developed load-bearing strengths greater than 5 kg/cm^2 (70 lb/in.^{2}) within one week. Rewetting results only in a temporary loss of strength until the sludge again dewatered. The inclusion of fly ash was beneficial to the dewatering process in all cases. In some cases, it was preferable to mix the ash with the sludge; in other cases there was greater advantage in having alternate layers of sludge (or sludge-fly ash mixtures) and fly ash, but generally, a drainage layer at the base (in these cases, fly ash) appreciably shortened the time for drainage and strength development. One of the most important conclusions is that preliminary partial dewatering by filtration or centrifugation is unnecessary. The clarifier underflow which is readily pumpable can be dewatered by underdrainage until load-bearing strengths have developed that are adequate to support heavy equipment.

9.3.2 Assessment of Underdrainage Technology

The use of underdrainage has demonstrated in laboratory tests the potential ability to provide environmentally sound disposal of untreated sludge. In most cases, underdrained sludge develops sufficient bearing strength (> 70 psi in a day or two after placement) to support construction equipment. In addition, the presence of an underdrainage system prevents the development of a hydraulic head over the subsoil, and only a minimal amount of leachate water penetrates the soil. This occurs only during the few years of filling. Thus, chemical pollution of groundwater is avoided, and, since supernate is not allowed to exist on the surface (except as noted in the following paragraph), no pollution by runoff is expected. These factors are discussed in the following example.

In this example of disposal procedure, it is assumed that FGD waste is placed in a closed basin to a depth of 30 to 40 ft, at the base of which is an underdrainage system which is buried under 1 ft or more of bottom ash, fly ash, sand, and gravel. The area being developed represents approximately one year of waste fill (about 30 acre/yr/1000-MW capacity during the first year of operation) and the waste may be placed by sluicing from a clarifier or trucked from a filter. If fly ash is removed upstream of the scrubber, it is added to the disposal site by alternate or simultaneous unloading with sludge; no mechanical mixing is necessary. Water that enters the basin, either with the solids during filling or by rainfall, is returned to the scrubber for reuse. The method is amenable

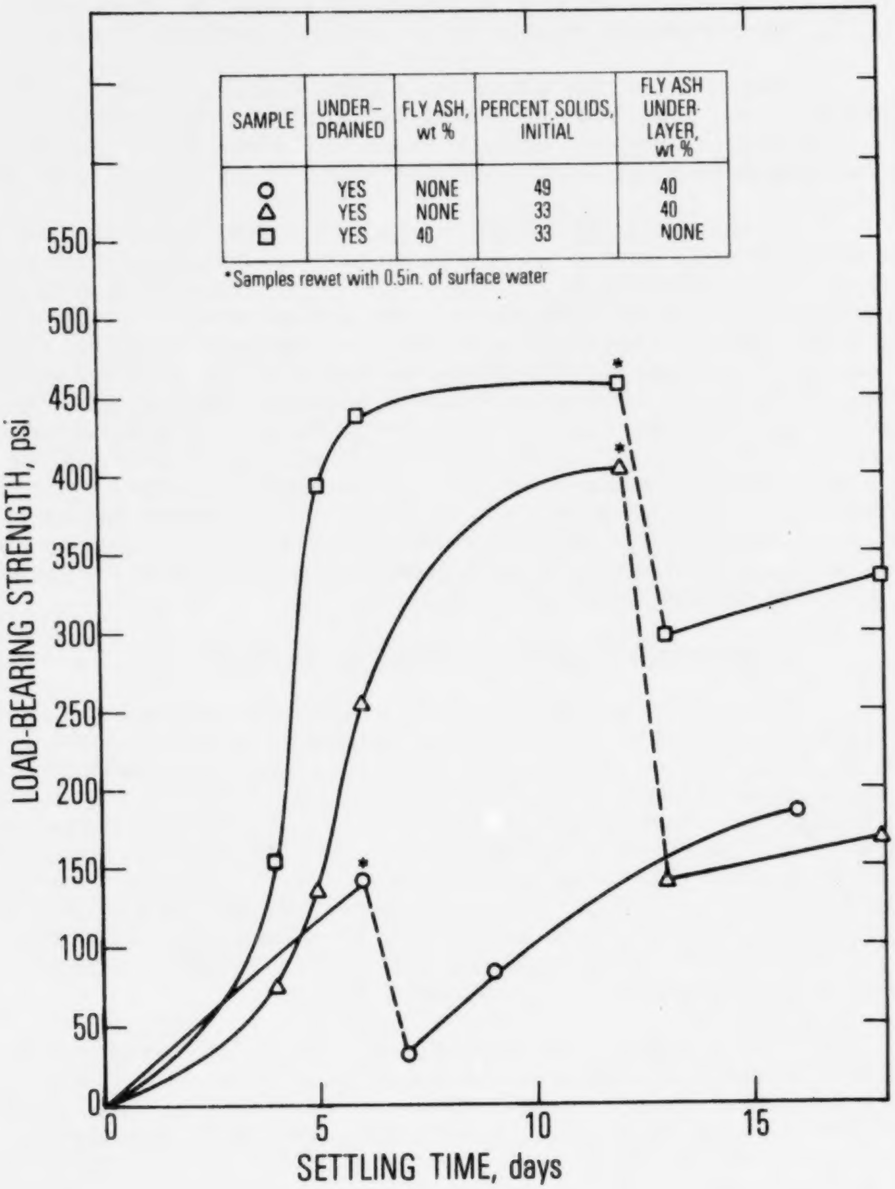


Figure 42. Effect of rewetting on development of bearing strengths of underdrained TVA Shawnee limestone sludge

to the continuous expansion of the disposal basin and simultaneous continuous land reclamation by covering with overburden. Since water evaporates more easily from damp solids than from a pond, advantages of this phenomena can be made by closing the underdrain valves and using the surface of the waste dried during the summer months to evaporate blowdown from a scrubber (if necessary). Normal disposal operations continue in an adjacent basin.

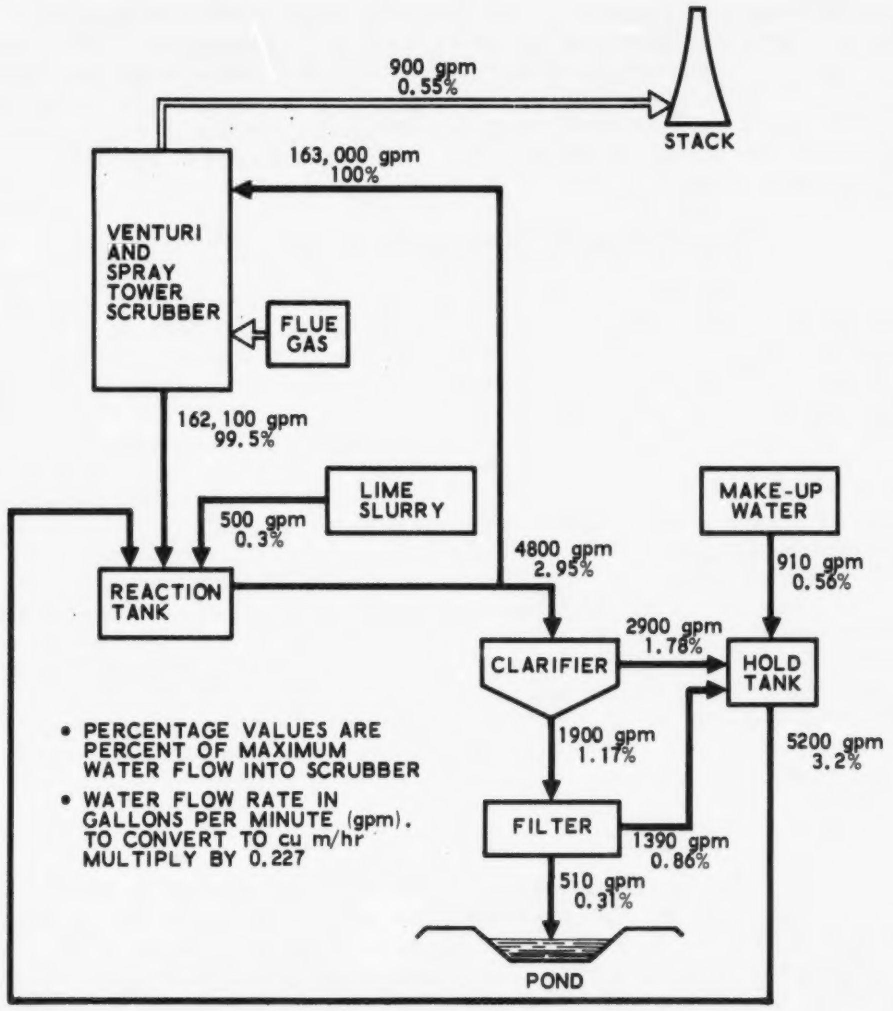
9.3.2.1 Water Balance in an Underdrained Disposal Site

The effect of water recirculated from an underdrained disposal site on the water and chloride ion balance of an FGD scrubber was calculated. The specific scrubber system chosen for the calculation was based on the TVA Shawnee 10-MWe venturi-spray tower scrubber using lime absorbent, and extrapolated to a 1000 MWe plant (Figure 43, Ref. 20). This basic system, without underdrainage, is representative of a tight, closed-loop water system which requires a total of 1410 gal/min (gpm) fresh makeup water to replace 900 gpm lost up the stack and 510 gpm lost by occlusion in the ponded waste containing 45 percent solids. In addition, supernate (1390 gpm) is returned to the scrubber loop from the pond; this results when the ponded clarifier underflow containing 18 percent solids settles to 45 percent solids. The chloride concentrations in the slurry from the scrubber and the supernate return are the same if the clarifier is not included; the amount of water to the disposal site and returned as supernate increases by 2900 gpm (the amount returned from a clarifier if used). This condition illustrated in Figure 43 was then modified to form a base case by including rainfall and returning unevaporated rainwater in the supernate from the pond to the plant.

9.3.2.1.1 Base Case

The base case assumed a disposal site of 30 acres, with no underdrainage, and the unevaporated rainfall returned in the supernate to the scrubber. A 30-acre operating site, with a depth of 30 ft, was chosen as a reasonable size in terms of operating efficiency and physical accessibility, with the sludge output of about one year's operation at 7000 hr per year being representative. The total amount of water falling onto a 30-acre area (at a rate of 48 in./year) is 41×10^6 gal/year or an average of 78 gpm. Based on a 30-acre surface area, a dry-bulb temperature of 68° F, and relative humidity of 50 percent, 85 gpm are evaporated (Figure 44). Although a 50 percent relative humidity and 78 gpm rainfall do not occur simultaneously, they are considered as concurrent average values for purposes of this preliminary analysis. Surge capacity to handle heavy rainfall conditions may be provided by the pond in service by limiting the underflow return during a portion of the fill period, or by using an adjacent pond not yet used or filled.

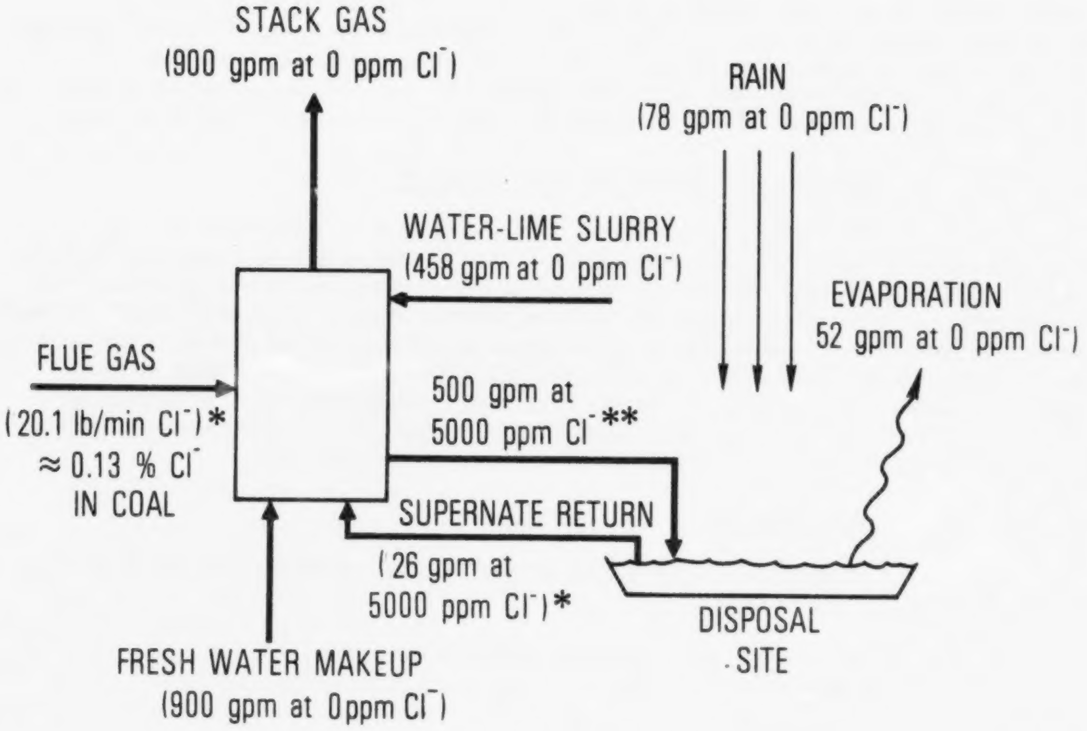
Data from the Shawnee evaluation (Ref. 3) indicate that a steady-state operating condition of 5000 ppm Cl^- may be expected in the pond input liquor and in the supernate.


900 gpm
0.55%
STACK
163,000 gpm
100%
VENTURI AND SPRAY TOWER SCRUBBER
FLUE GAS
162,100 gpm
99.5%
LIME SLURRY
500 gpm
0.3%
4800 gpm
2.95%
MAKE-UP WATER
910 gpm
0.56%
REACTION TANK
2900 gpm
1.78%
CLARIFIER
HOLD TANK
1900 gpm
1.17%
5200 gpm
3.2%
FILTER
1390 gpm
0.86%
510 gpm
0.31%
POND
• PERCENTAGE VALUES ARE PERCENT OF MAXIMUM WATER FLOW INTO SCRUBBER
• WATER FLOW RATE IN GALLONS PER MINUTE (gpm). TO CONVERT TO cu m/hr MULTIPLY BY 0.227

EXTRAPOLATED OPERATING CONDITIONS

LIQUID-TO-GAS RATIO: 54.0 gal/1000 cu ft
SCRUBBER EFFLUENT SOLIDS: 8 PERCENT
CLARIFIER UNDERFLOW SOLIDS: 18 PERCENT
WATER RETAINED IN SETTLED SLUDGE: 45 PERCENT SOLIDS
COAL: 3.4 PERCENT SULFUR
SO_2 REMOVAL EFFICIENCY: 90 PERCENT

Figure 43. Extrapolated water balance for venturi and spray tower scrubber system


STACK GAS
(900 gpm at 0 ppm Cl⁻)
RAIN
(78 gpm at 0 ppm Cl⁻)
WATER-LIME SLURRY
(458 gpm at 0 ppm Cl⁻)
EVAPORATION
52 gpm at 0 ppm Cl⁻)
FLUE GAS
(20.1 lb/min Cl⁻)*
≈ 0.13 % Cl⁻
IN COAL
500 gpm at
5000 ppm Cl⁻**
SUPERNATE RETURN
(26 gpm at
5000 ppm Cl⁻)*
DISPOSAL
SITE
FRESH WATER MAKEUP
(900 gpm at 0ppm Cl⁻)

IN*	OUT**
26 gpm x 8.5 x 0.005 = 1.1	500 gpm x 8.5 x 0.005 =
20.1	21.2 lb/min
21.2 lb/min	

Figure 44. Base case : ponding without underdrainage

9.3.2.1.2 Underdrained Case

Based on the characteristics of lime sludge remixed with fly ash, now being evaluated at Shawnee (Ref. 4), an additional 140 gpm is returned to the scrubber as underdrainage, in addition to the 1383 gpm returned in the base case (Figure 45). The 140 gpm represents additional water freed during the settling process (occurring because of underdrainage) when the solids content in the pond dewater from 45 to 60 percent solids. Again, assuming steady-state conditions with 22.0-lb/min Cl^- entering from the flue gas, a steady-state Cl^- concentration of 6900 ppm was calculated in the 1523 gpm underdrainage returning to the scrubber.

9.3.2.2 Summary - Underdrained Disposal

The disposal method just described is currently being evaluated on a small scale in the EPA/TVA Shawnee Field Disposal Evaluation Project (Ref. 4). In addition, operating strategies for a 30-year site using typical climatic conditions will be formulated. This technique, though not fully developed, appears to offer several desirable advantages regarding environmental pollution control as well as potential cost savings under specific conditions. Also, certain limiting conditions are associated with this technique. The advantages and limits to which underdrainage can be applied, as the method is now understood, are as follows.

9.3.2.2.1 Advantages

The advantages of the underdrained disposal method include the following:

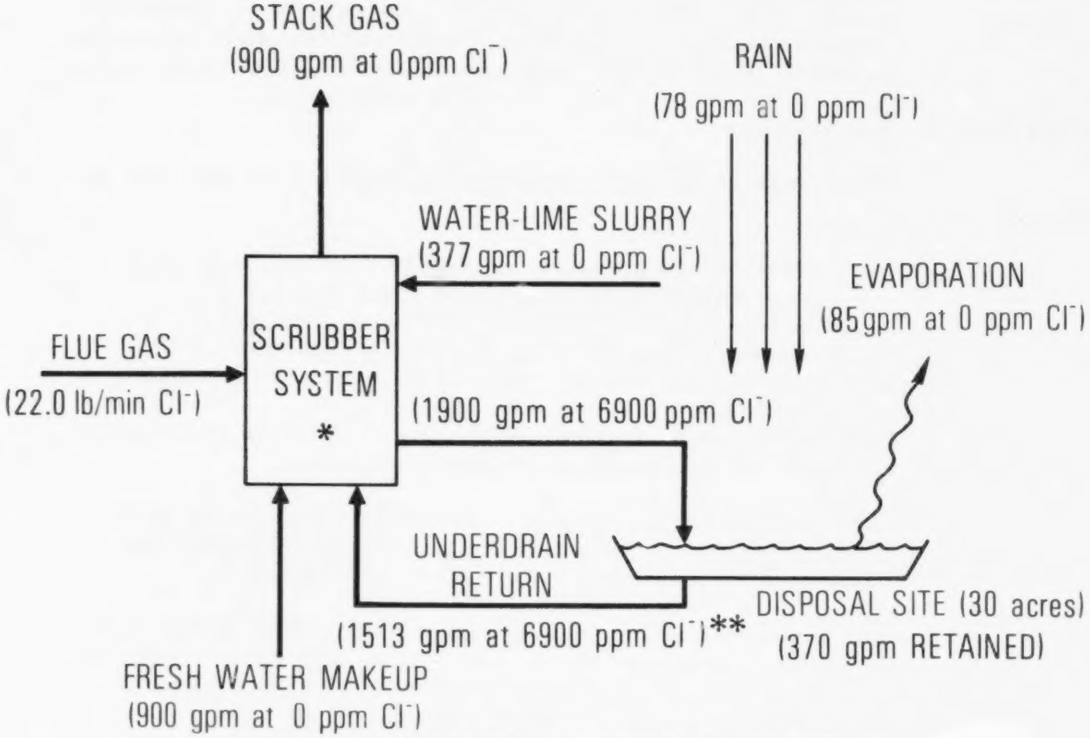
a. Dewatering equipment such as filters or clarifiers are not required; i.e., the sludge may be sluiced to the disposal site, and the underdrainage system is used to accomplish dewatering.

b. Underdrainage process is workable with sludges containing fly ash or without fly ash.

c. Load-bearing strengths in excess of 70 psi develop in a few days. The material loses some strength when rewetted by rainfall but regains its strength again in a few days.

d. Water balance of the scrubber loop can be maintained without detrimental effects, with proper design and management.

e. Underdrained basins can be used periodically as evaporation ponds (weather permitting)to evaporate scrubber blowdown if necessary.


STACK GAS
(900 gpm at 0 ppm Cl⁻)
RAIN
(78 gpm at 0 ppm Cl⁻)
WATER-LIME SLURRY
(377 gpm at 0 ppm Cl⁻)
EVAPORATION
(85 gpm at 0 ppm Cl⁻)
FLUE GAS
(22.0 lb/min Cl⁻)
SCRUBBER SYSTEM
*
(1900 gpm at 6900 ppm Cl⁻)
UNDERDRAIN RETURN
(1513 gpm at 6900 ppm Cl⁻)**
DISPOSAL SITE (30 acres)
(370 gpm RETAINED)
FRESH WATER MAKEUP
(900 gpm at 0 ppm Cl⁻)

CHLORIDE ION BALANCE IN SCRUBBER SYSTEM

	IN*	OUT**
UNDERDRAIN RETURN:	1523 gpm 8.5 x 0.069 = 89.3	1900 x 8.5 x 0.0069 =
FLUE GAS:	22.0	111.4 lb/min
	111.3 lb/min	

* Clarifier Included

** Concentration unchanged without clarifier

Figure 45. Ponding with underdrainage

f. Under most conditions, a pond lining is not required because a hydraulic head of any consequence does not exist. The material is continuously saturated, however; therefore, limitations on soil permeability and separation distance to the water table would need to be determined.

9.3.2.2.2 Limitations

The limitations of the underdrain disposal method are as follows:

a. An underdrained basin is limited in size because most of the rainfall is collected and routed through the underdrained system to the scrubber. Therefore, a modular approach wherein the disposal site is compartmented into basins, each containing, for example, approximately one year's output from the scrubber. For a 1000-MW system, operating at 7000 hr per year, 30 acres with a depth of 30 ft are required.

b. The disposal site must be reasonably close to the power plant to allow the installation of a closed-loop pipeline limited by the economics of efficient disposal.

c. An underdrainage system, with the potential of low cost by using a drainage blanket of bottom ash and/or gravel, sand, and fly ash has not been demonstrated. Such a development might result in significant savings as compared to a system of underdrainage pipes.

9.4 ASSESSMENT OF THE POTENTIAL CHEMICAL POLLUTION OF THE ENVIRONMENT BY ALTERNATIVE DISPOSAL METHODS

Pollution of groundwater by the action of rainwater percolating through FGD sludge is a major concern in the disposal of sulfur sludges. Laboratory experimentation has shown that relatively high concentrations of dissolved chemical species in the liquor from untreated sludges persist in the leachate until at least five PVD have passed through the sludge. Thereafter, the concentration depends on the solubility of the chemical phases in the sludge solids. The rate at which rainwater passes through FGD wastes has been measured in the range of 10^{-4} cm/sec, equivalent to soils of silty sand. The pollution of groundwater can be expressed as mass loading of pollutant that is carried by leaching water to groundwater.

The potential pollution that is possible from sludge when chemically treated by any of several processes can be reduced by several orders of magnitude. Improvement is accomplished by (1) the reduction of available chemical species in the treated sludge, (2) the reduction of rainwater available because of runoff, and (3) the elimination or reduction of the rate of water permeation through the chemically treated material. In nearly every case, the pollutant concentration of the leachate from treated sludges is less than one-half that of the leachate from untreated sludge when fresh material is placed in the disposal site. Additionally, the runoff from treated waste can be maximized and makes available much less than one-tenth of the rainfall for seepage, since the permeation coefficient of treated waste is typically reduced by at least an order of magnitude. Thus, the real pollutant migration measured by mass loading can be reduced by very large amounts.

The consequences of much lower permeability rates of chemically treated sludge are that many years will pass before five PVD in the sludge can reduce the leachate concentration to the level of the soluble salts. Therefore, while the pollution of groundwater by untreated sludge can be severe for a short period of time and low thereafter, the pollution potential of chemically treated sludge is not as severe but will be sustained for much longer periods of time. The latter case is more in consonant with nature, which weathers natural deposits slowly but constantly.

An evaluation of the amount of chemical pollutants that are available to the environment by leaching was determined from the results of the leaching data summarized in Section VII and the permeability data summarized in Section VI. Various examples illustrating the effects of sludge treatment, the effects of different subsoils, and the management of the site for different rainfall recharge rates are presented. The relative amounts of sludge constituents (TDS) released at the sludge base, for different modes of disposal were calculated (Table 33 and Figure 45). This analysis is based on correlations of laboratory results and Shawnee field condition data reported herein and in References 3 and 4. All the cases are indexed to an untreated slurry pond, namely, Case 1, in which the soil permeability coefficient is 10^{-5} cm/sec.

In assessing the effectiveness of chemical treatment, tests to determine permeability of chemically treated sludges were performed on cores extracted from the Shawnee field evaluation site. Constant-head permeability tests were run on (1) pulverized samples and (2) samples with and without visible cracks. Uncracked samples of the material had coefficients of permeability of about 10^{-7} cm/sec, and the pulverized and cracked samples had coefficients of approximately 10^{-5} cm/sec. Therefore, the effective coefficient of the treated material could be expected to be between 10^{-5} and 10^{-7} cm/sec. Assuming a conservative case (using a coefficient of 10^{-5}), an order of magnitude improvement in impermeability is realized compared to untreated sludges, which typically have a coefficient of about 10^{-4}.

The systematic reduction of standing water is illustrated in Cases 3 through 5, wherein the recharge rate is reduced compared to a

TABLE 33. BENEFITS OF CHEMICAL TREATMENT: CASE STUDIES FOR COMPARISON OF MASS RELEASE OF SLUDGE CONSTITUENTS FOR VARIOUS DISPOSAL ALTERNATIVES

Case	Disposal Method[a]	Surface Water	Sludge Condition[b]	Sludge Permeability, cm/sec
1	Ponded slurry	Constant supernate[c]	Untreated	10^{-4}
2	Ponded slurry	Constant supernate	Chemically treated	10^{-5}
3	Ponded cake	10-in/yr recharge[d]	Untreated	10^{-4}
4	Dewatered and ponded	10-in/yr recharge[d]	Chemically treated	10^{-5}
5	Landfill	1-in/yr recharge[e]	Chemically treated	10^{-5}

[a] Fill period = 5 yr; depth = 30 ft.

[b] Porosity (void volumetric fraction) = 0.67.

[c] Constant supernate assumes 1-ft depth of surface water.

[d] 10-in/yr recharge is unevaporated rainfall.

[e] 1-in/yr effective recharge resulting from seepage during runoff of rainfall.

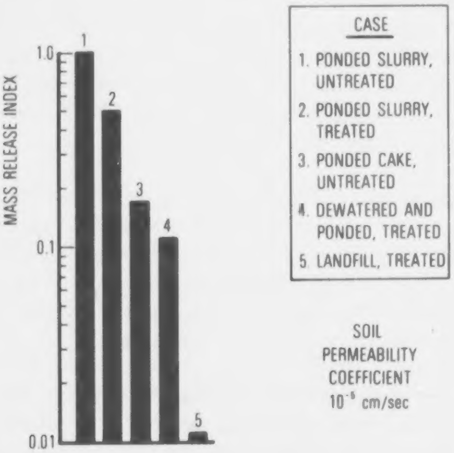


Figure 46. Comparison of mass release of sludge constituents for various disposal alternatives showing benefit of chemical treatment

available chemical species in the treated sludge, (2) the reduction of rainwater available because of runoff, and (3) the elimination or reduction of the rate of water permeation through the chemically treated material. In nearly every case, the pollutant concentration of the leachate from treated sludges is less than one-half that of the leachate from untreated sludge when fresh material is placed in the disposal site. Additionally, the runoff from treated waste can be maximized and makes available much less than one-tenth of the rainfall for seepage, since the permeation coefficient of treated waste is typically reduced by at least an order of magnitude. Thus, the real pollutant migration measured by mass loading can be reduced by very large amounts.

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5	Landfill	1-in/yr recharge[e]	Chemically treated	10^{-5}

[a] Fill period = 5 yr; depth = 30 ft.

[b] Porosity (void volumetric fraction) = 0.67.

[c] Constant supernate assumes 1-ft depth of surface water.

[d] 10-in/yr recharge is unevaporated rainfall.

[e] 1-in/yr effective recharge resulting from seepage during runoff of rainfall.

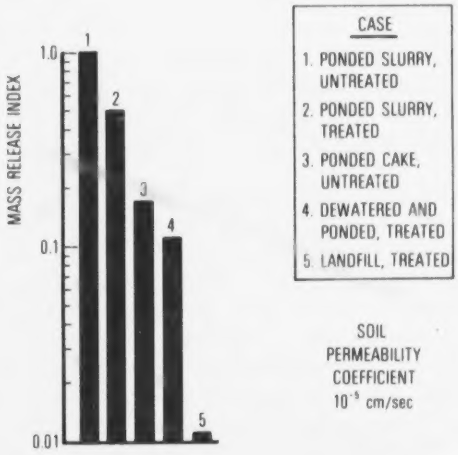

Figure 46. Comparison of mass release of sludge constituents for various disposal alternatives showing benefit of chemical treatment

ponded slurry. If only unevaporated rainfall is allowed to recharge, the mass release into the subsoil is reduced by a factor of about 5 (Case 3 versus 1, and Case 4 versus 2).

The significance of eliminating standing water by runoff is also shown. If it is assumed that 10 percent of the net rainfall is recharged, then a one order of magnitude reduction is achieved relative to a dewatered and ponded treated waste (Case 5 versus 4), and two to three orders of improvement are seen, depending on soil permeability, when comparing the mass seepage from a chemically treated site to that of a ponded untreated site (Case 5 versus 1). In addition, compacting the treated materials during the site filling may reduce crack formation so that an effective coefficient of permeability better than 10^{-5} cm/sec may be realized.

Case 2 (Figure 46) considers chemically treated sludges disposed of in such a manner that a hydraulic head exists on the site at all times. The mass release for such a case is approximately 1/2 to 1/20 of that of an untreated slurry pond depending on subsoil permeability. Sites of this type may seep to an adjacent stream or water table, which may reduce the concentration of constituents by mixing. Historical data regarding the stream and water table characteristics and quality, as well as monitoring, may be mandatory for sites of this type to assure environmental acceptability.

SECTION X

DISPOSAL COST ESTIMATES

Cost estimates for ponding, chemical treatment, and landfilling have been made and reported by Aerospace on several occasions. During recent studies associated with the U.S. Environmental Protection Agency (EPA) Shawnee field disposal evaluation project, Aerospace cost estimates were made of chemical treatment disposal and were reported in the initial report on that study (Ref. 3). The Aerospace cost estimates for lined-pond disposal and chemical treatment disposal were presented in the initial and second progress reports on the sludge disposal study (Refs. 1 and 2) and at the EPA 1974, 1976, and 1977 flue gas desulfurization symposiums (Refs. 8 through 10). These estimates were updated to July 1977 costs in a more recent report prepared for EPA on new source performance standards (Ref. 21). In that update refinements were made to reflect more current data on coal content, plant efficiency, operating conditions, and land costs. A comparison of the conditions for the current estimates with the previous baseline assumptions are shown in Table 34.

10.1 ECONOMICS OF DISPOSAL PROCESSES

The four flue gas desulfurization (FGD) waste disposal methods selected for economic evaluation were as follows:

a. Ponding of untreated wastes using a flexible elastomeric liner.

b. Ponding of untreated sludges using indigenous clay.

c. Chemical treatment and landfill disposal.

d. Forced oxidation of sulfite sludge to gypsum and landfill disposal.

10.1.1 Ponding of Untreated Wastes

Several waste pond sites currently in operation employ flexible elastomeric liners and sites lined with indigenous clay (impervious) soil; however, only one elastomeric lined pond is reported to contain FGD sludge.

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TABLE 34. COMPARISON OF CONDITIONS FOR CURRENT DISPOSAL COST ESTIMATES WITH PREVIOUS ESTIMATES

Condition	Previous	Current
Dollar Base	1975	July 1977
Plant Characteristics	1000 MWe, 0.88-lb coal/kWh	1000 MWe, 0.75-lb coal kWh
Coal Burned	3.0% sulfur, 10,560 Btu/lb, 12% ash	3.5% sulfur, 12,000 Btu/lb, 14% ash
Annual Operating Hours	4380 (30-yr av)	4380 (30-yr av)
Plant and Disposal Site Lifetime	30 yr	30 yr
SO_2 Removal, with Limestone Absorbent	85%	90%
Sludge Generated	5.475×10^5 short tons/yr (dry)	4.798×10^5 short tons/yr (dry)
Limestone Utilization	65%	80%
Average Annual Capital Charges, 30-yr av	18%	18%
Cost of Land Used for Disposal	$1000/acre; all land assumed purchased initially; sludge depth, 30 ft	$5000/acre; all land assumed purchased initially; sludge depth 30 ft
Land Depreciation	Total depreciation in 30 yr; straight line basis	Total depreciation in 30 yr; straight line basis
Disposal Site	Within one mile of plant	Within one mile of plant

Since previous work (Ref. 2) has shown that the optimum pond depth for this type of disposal is 30 ft, which is the depth at which pond construction and land costs are optimum with respect to the cost of liner material, the results are reported on the basis of a 30-ft depth of sludge.

Commercial materials which are considered typical of the price range of installed liners, i.e., PVC (20-mil thickness) and Hypalon (30-mil thickness) were used in this study. The least expensive of these two materials, i.e., PVC-20, was selected for this analysis, which is summarized in Table 35. The indigenous soil is assumed to be impervious, with a permeability coefficient of 10^{-6} cm/sec or better.

10.1.2 Chemical Treatment and Disposal

The cost of chemical treatment and disposal of FGD sludge in a landfill was estimated in March 1976 (Ref. 3). At that time, estimates of total disposal costs were made for three chemical treatment processes, i.e., Dravo, IU Conversion Systems, and Chemfix, for a 1000-MW plant based on 1975 dollars. With this work as a basis, cost estimates have been updated for the current conditions referenced in Table 34 and summarized in Table 35.

10.1.3 Economics of Conversion to Gypsum

The cost of producing gypsum as a by-product from line or limestone 1000-MWe scrubbing processes has been reported for mid-1977 by Aerospace (References 1 and 11). The estimate included the costs required to incorporate the forced oxidation processing into a basic lime or limestone scrubber system. The fly ash was assumed to be separated in electrostatic precipitators. However, the cost of ESP's was not charged to the cost of producing the gypsum. Alternatively, the fly ash could be scrubbed in a two-stage venturi-absorber, forced oxidation system. On the basis of the power plant and scrubbing conditions shown in Table 34, 2.65×10^5 tons of ash-free gypsum (dry basis) would be produced annually.

The capital equipment costs to produce gypsum in a new 1000-MWe installation, scrubbing flue gas from 3.5 percent sulfur coal, and removing 90 percent SO_2, is $\$10.09 \times 10^6$ or $10.00/kW. The estimates, which include the cost of oxidizing the waste to gypsum and the disposal of the gypsum combined with 222,000 short tons of ash, are summarized in Table 35.

10.2 COST COMPARISON

A comparison of costs for the various forms of disposal is given in Table 35. In addition to presenting the costs in mills/kWh, costs are also presented in terms of cost per ton dry sludge and cost per ton of coal burned. The disposal cost for gypsum includes the additional cost of forced oxidation of the sulfite slurry, and, for ease of comparison, the gypsum cost is converted to the cost of an equivalent amount of sludge.

TABLE 35. DISPOSAL COST COMPARISONS[a]

Cost Basis, Mid-1977 $	Ponding		Landfill-Chemical Treatment	Gypsum[b]
	Liner Added	Indigenous Clay		
Mills/kWh	0.80	0.55	1.05	1.10
$/Ton Sludge (Dry)	7.25	4.90	9.70	10.30[c]
$/Ton Coal	2.20	1.50	2.95	3.10

[a] See Table 34 for all referenced conditions.

[b] 100% limestone utilization for gypsum case; all others, 80%.

[c] Cost of forced oxidation and disposal of gypsum sludge (including fly ash) in an indigenous clay-lined pond is converted to cost/ton of equivalent FGD nonoxidized sludge including fly ash. To convert to cost/ton of gypsum including fly ash, divide by 1.08.

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APPENDIX

CRYSTAL MORPHOLOGY

For each of the sludges evaluated in this report period, a portion was selected, dried, and prepared for scanning electron micrographic (SEM) examination. The dry powders were sprinkled onto an aluminum sample holder and vapor-coated with a thin layer of conducting carbon before insertion into the SEM viewing chamber. A series of photomicrographs were taken of each sludge sample, from which typical examples of the crystalline morphology of the solids content were selected. The photomicrographs and description of the solid particulate material characteristic of each sludge are presented in the following text.

A. 1 TVA SHAWNEE LIME SLUDGE, RUN F, WITHOUT FLY ASH

The characteristics of the solids content of the Tennessee Valley Authority (TVA) Shawnee venturi spray tower system using lime absorbent and containing no fly ash is shown in Figure A-1. The sulfur phase is represented by calcium sulfite rosettes that range between about 15 and 30-μm diam with the median cluster size about 20-μm diam. Individual platelet size was typically 5 μm in its longest dimension and rarely exceeded 10 μm. The platelet thickness was typically 0. 1 to 0. 5 μm. These particle characteristics are nearly identical to the characteristics of particles previously observed (Ref. 1) from this scrubber system. The primary difference between this sludge and those observed previously is the near absence of fly ash, and it may be presumed that differences in physical behavior may be ascribed to fly ash. In the present sludge sample, very fine fly ash particles were occasionally observed, but they constituted less than one percent of the sludge sample.

A. 2 GPS SCHOLZ DOUBLE ALKALI SLUDGE, WITHOUT FLY ASH

The solids content of the sludge from the Gulf Power Service (GPS) Scholz double alkali scrubbing facility are shown in Figure A-2. This sludge was comprised of very fine particulates agglomerated in clusters. The fine particulates were calcium sulfite hemihydrate, with dimensions in the range of 1 μm along an edge and thickness of 0. 05 to 0. 1 μm. Cluster sizes

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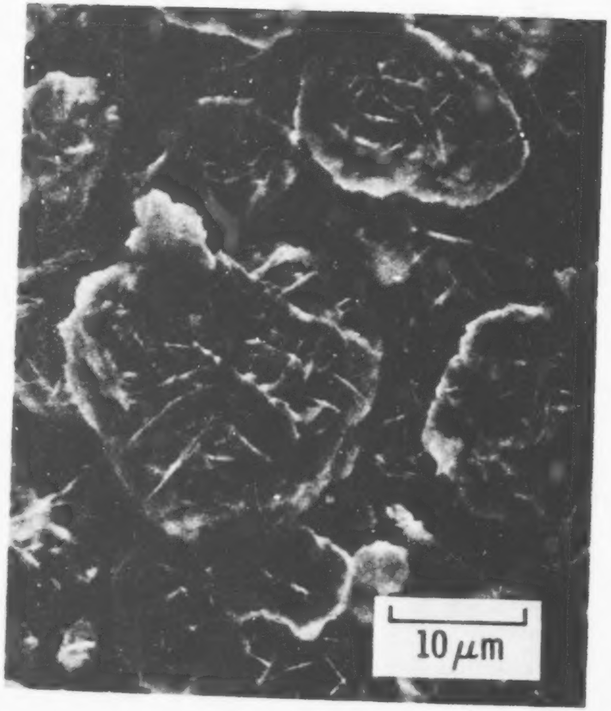

Figure A-1. Shawnee, venturi and spray tower, lime sludge solids, no fly ash, X2000

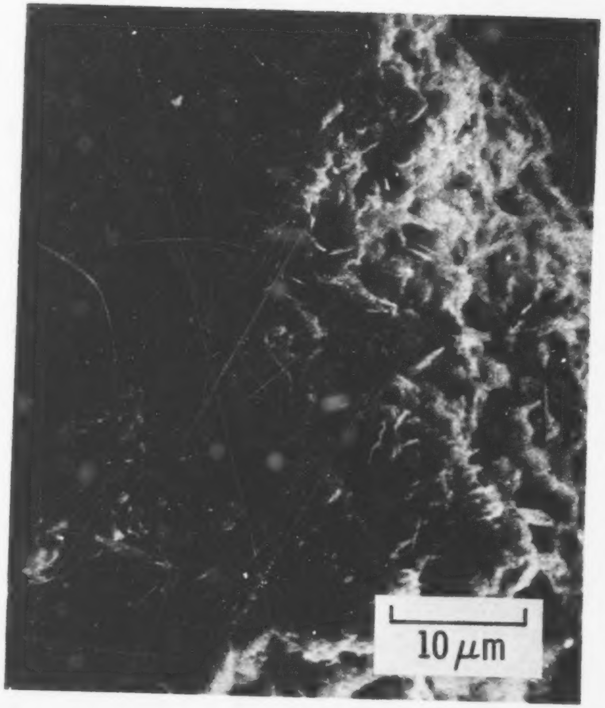

Figure A-2. Scholz double-alkali sludge solids, no fly ash, X2000 ranged from individual particles up to agglomerates as large as 50 μm in diameter. Most agglomerates, however, were about 10 to 20 μm in diam. In contrast to the rosette clusters observed in the TVA Shawnee lime sludge, the particles of the Scholz sludge did not form well-structured agglomerates but were more randomly formed and showed more clear evidence of intergrowth, as observed frequently with gypsum sludges. From the nature of the intergrowth integrity, it is presumed that the physical behavior of this sludge resembles a material with a particle size and broad particle range of the agglomerates rather than that of the fine particle size of the individual particulate.

A.3 GPS SCHOLZ DOUBLE ALKALI SLUDGE, WITH FLY ASH

The GPS Scholz double alkali sludge solids which contained fly ash are shown in Figure A-3. This sample had sulfur phase agglomerates identical to those described in the previous subsection. In addition, there were fly ash particles that ranged from submicron to about 25-μm diam, with the majority of the fly ash particles in the range of 10- to 20-μm diam. Many of the smaller particles were shaped as prolate spheroids, typical of cyclone boilers.

A.4 LG&E PADDY'S RUN SLUDGE, CARBIDE LIME

The sludge solids from the Louisville Gas and Electric (LG&E) Paddy's Run station are shown in Figure A-4. The characteristics of this sludge differ from others in that few agglomerates were formed. Nevertheless, individual particle sizes were small, typically ranging from 0.1 to 5 μm along an edge. Thickness dimensions of 0.05 μm and less were observed. Some agglomerates were observed, but few were larger than 5 μm in a major dimension. Among all sludges characterized, this sludge contained the finest, dispersed particle distribution thus far observed. Fly ash particles were also observed in the sludge, and their particle size range was typically 0.1 to 5 μm, also, with a mean particle size of about 1 μm. The observed frequency of fly ash in the SEM micrographs was less than that indicated by chemical analyses and may be caused by the obscuration of the fly ash by the fine, dispersed sulfur phase. The physical behavior of this sludge is not expected to resemble any other among those tested in this report but resemble more the behavior of the double alkali sludges with fine particle sizes previously reported (Ref. 1).

A.5 TVA SHAWNEE LIMESTONE SLUDGE, WITHOUT FLY ASH, BLOCKY CRYSTALS

During a series of ash-free test runs of the turbulent contact absorber (TCA) at the TVA Shawnee station, limestone absorbent was used and scrubber operating parameters, such as slurry solids, hold tank size, and reaction tank residence time, were varied. A SEM of a sample analyzed is shown in Figure A-5. This is not considered a typical sample. Nonetheless, it is of interest because of the "blocky" shape of the sulfite crystals (10 to

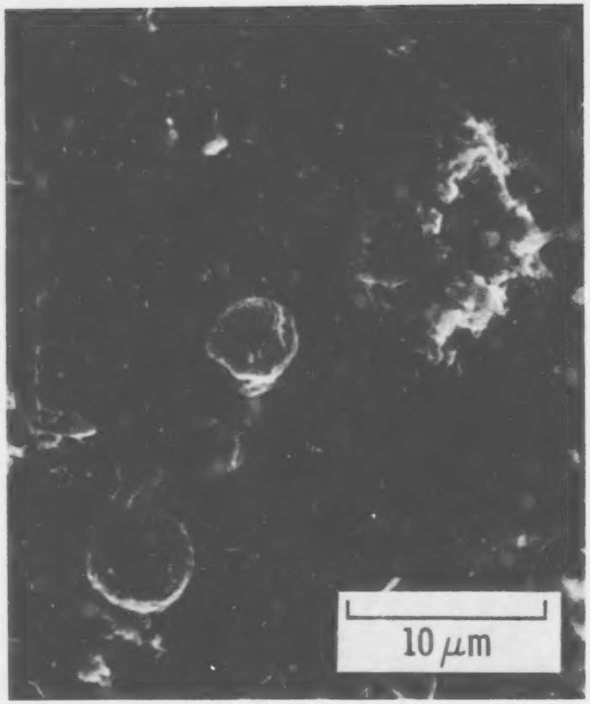

Figure A-3. Scholz double-alkali sludge solids with fly ash, X3000

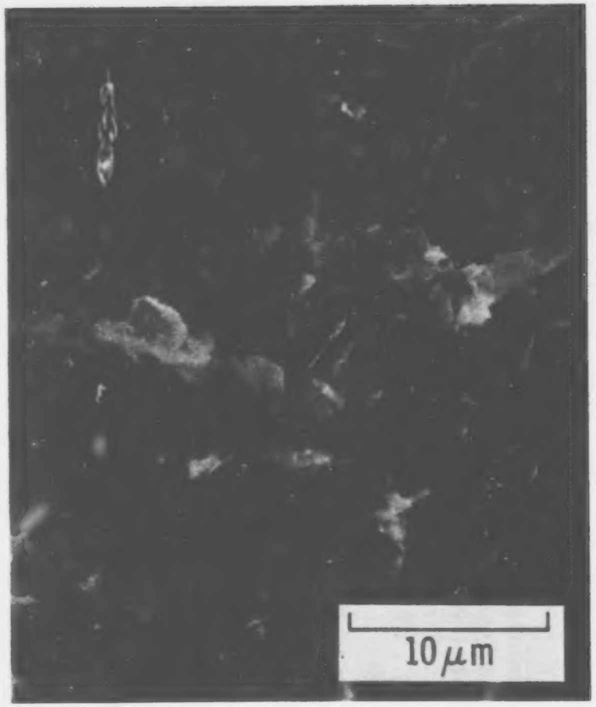

Figure A-4. Paddy's Run carbide-lime sludge solids with fly ash, X3000

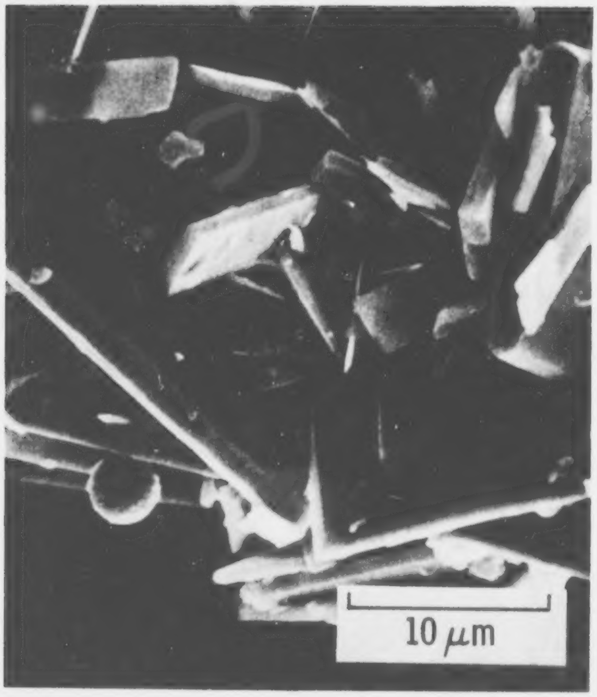

Figure A-5. Shawnee TCA limestone sludge solids, no fly ash (not considered typical) X3000

20 μm and 2 to 4 μm thick), which displayed improved draining and load-bearing strength properties compared to limestone sludge samples from the same scrubber, which typically produces platelets considerably smaller than the crystals in Figure A-5.